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[Jour. Indian Chem. Soc., Vol. 30, No. 6, 1953]

STUDIES IN FRIES MIGRATION. PART IX. FRIES MIGRATION OF THE ACETYL ESTERS OF 2:4-DIHYDROXY-5-SUBSTITUTED BENZOIC ACIDS AND THEIR METHYL ESTERS

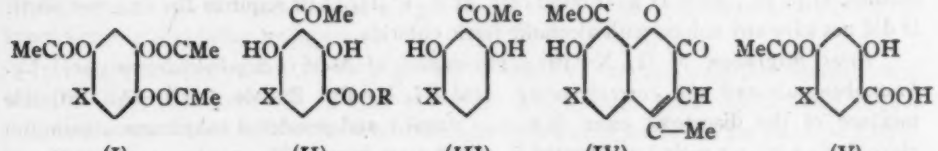
By J. I. Setalvad and N. M. Shah

The Fries isomerisation of the acetyl esters of 5-bromo-, 5-chloro- and 5-nitro-2:4-dihydroxybenzoic acids and their methyl esters has been investigated. It is found that except in the case of 5-nitro-β-resorcylic acid derivatives, the migration takes place in the γ-position of the resorcinol nucleus, while in the case of the nitro compounds, the migration does not take place, the de-acetylated compounds being recovered.

In continuation of the work described in the previous part (this *Journal*, 1952, **29**, 915) the Fries isomerisation of the acetyl esters of 5-bromo-, 5-chloro- and 5-nitro-β-resorcylic acid and their methyl esters has been investigated.

Methyl 2:4-diacetoxy-5-bromobenzoate (I, X=Br) on the Fries migration at 120° and 140° gave methyl 2:4-dihydroxy-3-acetyl-5-bromobenzoate and the corresponding acid (II, X=Br, R=Me and H), some hydrolysis occurring during the migration. The keto-ester was hydrolysed to the keto-acid (II, X=Br, R=H) which on decarboxylation gave 2-acetyl-4-bromoresorcinol (III, X=Br), which smoothly underwent Pechmann condensation with ethyl acetoacetate yielding 8-acetyl-7-hydroxy-6-bromo-4-methylcoumarin (IV, X=Br), identical with the migration product of 7-acetoxy-6-bromo-4-methylcoumarin (unpublished).

The migration at 170°-180° gave only the keto-acid (II, X=Br, R=H), the ester being hydrolysed completely during the migration. For comparison, methyl 2:4-dihydroxy-5-bromobenzoate was subjected to Friedel-Crafts acetylation, the product (II, X=Br, R=Me), obtained in good yield, being identical with the above migration product.



(I) (II) (III) (IV) (V)

4-Acetoxy-2-hydroxy-5-bromobenzoic acid (V, X=Br) at 145° isomerised to 2:4-dihydroxy-3-acetyl-5-bromobenzoic acid (II, X=Br, R=H) which (*i*) on decarboxylation gave 2-acetyl-4-bromoresorcinol (III, X=Br) and (*ii*) on esterification with methyl alcohol gave the ester (II, X=Br, R=Me), identical with the above migration product. It is interesting to note that below 145° no migration takes place; while at 170° the keto-acid (II, X=Br, R=H) is obtained in diminished yield.

Similarly methyl 2:4-diacetoxy-5-chlorobenzoate (I, X=Cl) and 4-acetoxy-2-hydroxy-5-chlorobenzoic acid (V, X=Cl) were subjected to the Fries isomerisation and the corresponding 3-acetyl-chloro derivatives were obtained.

It is generally known that nitro group in *ortho* or *para* position completely inhibits the Fries reaction (Rosenmund and Schnurr, *Annalen*, 1928, **460**, 56). However, Brown (*J. Amer. Chem. Soc.*, 1946, **68**, 873) was successful in obtaining 3-nitro-4-hydroxy-acetophenone by the migration of *o*-nitrophenyl acetate. He also carried out the Friedel-Crafts acetylation of *o*-nitrophenol with acyl halides.

2:4-Diacetoxy-5-nitrobenzoate (I, X=NO_2) and 4-acetoxy-2-hydroxy-5-nitrobenzoic acid (V, X=NO_2) were subjected to Fries migration, under various conditions, but only de-acetylation was found to take place.

The results thus show that chlorine and bromine as substituents in β-resorcylic acid have no retarding effect, the migration taking place in the γ-position of the resorcinol nucleus; while the nitro group in the same position inhibits the reaction. Incidentally the work provides a direct and convenient method for the synthesis of 2-acetyl-4-chloro- or bromo-resorcinols (III, X=Cl or Br).

EXPERIMENTAL

Fries Migration of Methyl 2:4-Diacetoxy-5-bromobenzoate

2:4-Dihydroxybenzoic acid (β-resorcylic acid) was prepared from resorcinol according to Nierenstein and Clibbens (Org. Syn. Coll. Vol. II, 1946, p. 557).

2:4-Dihydroxy-5-bromobenzoic acid was prepared according to Sandin and McKee (*ibid.*, p. 100). The bromo-acid (50 g.) was esterified by methyl alcohol (150 c.c.) containing concentrated H_2SO_4 (12 c.c.) by refluxing for 18 hours; the ester obtained was crystallised from dilute alcohol (50%) as clusters of needles, m.p. 140°, yield 30 g. (Found: Br, 32.2. $C_8H_7O_4Br$ requires Br, 32.4 per cent).

Methyl 2:4-Diacetoxy-5-bromobenzoate (I, X=Br) was obtained from methyl 2:4-dihydroxy-5-bromobenzoate (15 g., 1 mol.), acetic anhydride (20 c.c., 2.2 mols.) and fused sodium acetate (15 g.) by heating on a water-bath for 3 hours. The product obtained was crystallised from minimum amount of ice-cold alcohol in clusters of silky needles, m.p. 56°, yield 11 g. (Found: Br, 24.0. $C_{13}H_{11}O_6Br$ requires Br, 24.2 per cent). It did not give any colour with alcoholic ferric chloride.

Fries Migration of (I, X=Br): *Formation of Methyl 2:4-Dihydroxy-3-acetyl-5-bromobenzoate and the corresponding Acid* (II, X=Br; R=Me & H).—An intimate mixture of the diacetoxy ester (3.5 g., 1 mol.) and powdered anhydrous aluminium chloride (4.5 g., 3.3 mols.) was heated at 120° for an hour. The evolution of HCl gas began at 70°-75° and slackened within half an hour. The cold reaction mixture was treated with dilute sodium bicarbonate solution (5%) when a part of it dissolved with effervescence. The insoluble portion was crystallised from alcohol in pale yellow, lustrous needles, m.p. 145°, yield 1.5 g. (Found: Br, 27.5. $C_{10}H_9O_5Br$ requires Br, 27.7 per cent).

The bicarbonate filtrate on acidification gave a colorless solid, crystallised from hot water containing a few drops of acetic acid as needles, m.p. 224° (decomp.), yield 0.5 g. (Found: Br, 29.0; equiv. 273.0. $C_9H_7O_5Br$ requires Br, 29.1 per cent. Equiv., 275.0).

Both the keto-ester and the acid dissolved in alkali with a bright yellow colour and gave a red colour with alcoholic ferric chloride.

The above migration, when repeated at 140°, gave the same products, the yield of the keto-acid being more than the corresponding keto-ester. The migration at 175° gave only the keto-acid in diminished yield. The migration was also carried out using nitrobenzene as the solvent at 100° for 1 hour or at room temperature for 24 hours. The brownish oil obtained after steam-distillation of nitrobenzene was extracted with alkali solution (5%). The alkaline extract on acidification gave a solid which was found to be the mixture of the keto-ester and the acid (II, X=Br, R=Me and H). They were found to be identical (mixed m.p.) with the migration products obtained before.

Friedel-Crafts Acetylation of Methyl 2:4-Dihydroxy-5-bromobenzoate: Formation of II (X=Br, R=Me & H).—Powdered anhydrous aluminium chloride (4.0 g.) was dissolved in dry nitrobenzene (40 c.c.). The solution was cooled and methyl 2:4-dihydroxy-5-bromobenzoate (3 g.) was added to it in small instalments. The reaction mixture after adding acetic anhydride (25. c. c.) with shaking and cooling was left overnight at room temperature ($CaCl_2$ guard tube). It was then heated at 110° on an oil-bath for 4 to 5 hours. The keto-ester (II, X=Br, R=Me) (1.8 g.) and the acid (II, X=Br, R=H) (0.4 g.) were obtained and identified by directly comparing them with the migration products.

The following derivatives of the keto-ester (II, X=Br, R=Me) were prepared. The *semicarbazone* crystallised from alcohol in needles, m.p 261° (decomp.). The *monoacetyl derivative*, prepared by acetic anhydride-sulphuric acid drop method, crystallised from dilute alcohol in needles, m.p. 98°. (Found: Br, 23.9. $C_{13}H_{11}O_6Br$ requires Br, 24.2 per cent). It dissolves in alkali and gives a red colour with alcoholic ferric chloride.

The *oxime*, prepared by the usual method, crystallised from dilute alcohol as fibrous needles, m.p. 218° (decomp.).

Hydrolysis of (II, X=Br, R=Me).—The solution of the keto-ester (1 g.) in sodium hydroxide (20 c.c., 10%) was left overnight at room temperature. On acidification the solid obtained was collected and crystallised from very dilute acetic acid as colorless needles, m.p. 225° (decomp.), yield 0.7 g., mixed m.p. with 2:4-dihydroxy-3-acetyl-5-bromobenzoic acid being undepressed.

Decarboxylation of (II, X=Br, R=H): *Formation of 2-Acetyl-4-bromoresorcinol* (III, X=Br).—The keto-acid (3 g.), water (150 c.c.), acetic acid (5 c.c.) and a few drops of concentrated hydrochloric acid were refluxed on a sand-bath for 18 to 20 hours. The hot yellow solution was filtered off to remove tarry impurities. The filtrate on cooling deposited yellow needles. They were collected, washed with bicarbonate solution, and crystallised from very dilute alcohol as clusters of bright yellow needles, m.p. 143°, yield 1.0 g. (Found: Br, 34.3. $C_8H_7O_3Br$ requires Br, 34.6 per cent) It is very soluble in alcohol but less easily in water, benzene, chloroform and petroleum ether. It dissolves in alkali with a bright yellow colour and gives a green colour with alcoholic ferric chloride. Its mixed melting point with the hydrolysis product of 8-acetyl-7-hydroxy-6-bromo-4-methylcoumarin (unpublished) was undepressed.

Pechmann Condensation of (III, X=Br) : *Formation of* (IV , X=Br).—A mixture of the bromo-ketone (III, X=Br; 0.5 g.), ethyl acetoacetate (1 c.c.) and H_2SO_4 (75%, 3 c.c.) was left overnight at room temperature and then decomposed by ice-cold water.

The solid obtained was collected and crystallised from alcohol as small yellow needles, m.p. 200°. (Found : Br, 26.8. $C_{12}H_9O_4Br$ requires Br, 26.9 per cent). Its mixed m.p. with the migration product of 7-acetoxy-6-bromo-4-methylcoumarin (*loc.cit.*) was undepressed. It gives a red colour with alcoholic ferric chloride and dissolves in alkali with a non-fluorescent yellow colour.

Fries Migration of 2-Hydroxy-4-O-Acetyl-5-bromobenzoic Acid

2-Hydroxy-4-*O*-acetyl-5-bromobenzoic acid (V, X=Br) was prepared by acetic anhydride-sulphuric acid drop method. The buff coloured solid obtained was crystallised from acetic acid as lustrous needles, m.p. 143°, yield 9 g. (Found: Br, 29.4; equiv., 273.1. $C_9H_7O_5Br$ requires Br, 29.2 per cent. Equiv., 275.0). It gives a purple colour with alcoholic ferric chloride and dissolves in alkali without any colour.

Fries Migration of (V, X=Br): *Formation of* (II, X=Br, R=H).—The acetoxy-acid (V, X=Br) (5.5 g., 1 mol.) and anhydrous aluminium chloride (8.8 g., 3.3 mols.) were heated at 145°-150° for one hour. The solid product obtained was extracted with sodium bicarbonate solution (5%) when most of it dissolved with effervescence. The bicarbonate filtrate on acidification gave a solid, which was crystallised from hot water containing a few drops of acetic acid in needles, m.p. 224° (decomp.), yield 3.0 g. (Mixed m.p. with the same acid obtained before was undepressed).

The migration at 170° for one hour gave the same keto-acid in poor yield ; with nitrobenzene no migration took place.

The following derivatives of (II, X=Br, R=H) were prepared.

The *methyl ester* was prepared by refluxing the keto-acid (1 g.), methyl alcohol (10 c.c.) and a few drops of concentrated H_2SO_4 for 18 to 20 hours, and crystallised from alcohol in needles, m.p. 145° (0.3 g.) ; its mixed melting point with the keto-ester (II, X=Br, R=Me) obtained before was undepressed.

The *semicarbazone* crystallised from dilute alcohol in needles, m.p. 230° (decomp.).

The *monoacetyl* derivative crystallised from dilute alcohol as truncated needles, m. p. 159°. (Found: Br, 25.1. $C_{11}H_9O_6Br$ requires Br, 25.2 per cent). It gives a red colour with alcoholic ferric chloride.

Fries Migration of Methyl 2:4-Diacetoxy-5-chlorobenzoate

For sake of brevity, the experimental details have been omitted in this case as they are generally identical with those of the corresponding bromo compounds, already described.

2:4-*Dihydroxy-5-chlorobenzoic acid* was prepared according to Pectynin and Kuchina (*Chem. Abs.*, 1948, **42**, 4550).

Methyl 2:4-dihydroxy-5-chlorobenzoate was prepared by esterifying the above acid with excess of methyl alcohol in presence of H_2SO_4 (conc.) on a water-bath for 20 hours and crystallised from 50% alcohol as colorless truncated needles, m.p. 165°, yield 55%. (Found: Cl, 17.3. $C_8H_7O_4Cl$ requires Cl, 17.5 per cent) .

Methyl 2:4-diacetoxy-5-chlorobenzoate (I, X=Cl) crystallised from alcohol as colorless shining plates, m.p. 102° (Found: Cl, 12.1. $C_{12}H_{11}O_6Cl$ requires Cl, 12.4 per cent).

Fries Migration of (I, X=Cl) *and Friedel-Crafts Acetylation of Methyl 2:4-Dihydroxy-5-chlorobenzoate* : *Formation of* (II, X=Cl).—A mixture of the ester (I, X=Cl ; 3 g., 1 mol.) and aluminium chloride (4.5 g., 3.3 mols.) was heated at 130°-135° for one hour. The products were separated by the bicarbonate treatment. The insoluble portion was collected and crystallised from alcohol as slender, silky needles, m.p. 124°, yield 1.5 g. (Found: Cl, 14.37. $C_{10}H_9O_5Cl$ requires Cl, 14.52 per cent). The bicarbonate filtrate on acidification gave a solid, crystallised from very dilute acetic acid as greenish yellow, fibrous needles, m.p. 232° (decomp.), yield 0.8 g. (Found: Cl, 15.29; equiv., 232.6. $C_9H_7O_5Cl$ requires Cl, 15.40 per cent. Equiv., 230.5).

Both the keto-ester and the acid dissolve in alkali with a bright yellow colour and give a red colour with alcoholic ferric chloride.

The migration at 100° for one hour gave only the unchanged diacetoxy ester, while at 170° the keto-acid with traces of the corresponding ester was obtained. The migration was carried out with nitrobenzene as a solvent, the same products being obtained.

On Friedel-Crafts acetylation of the ester the keto-ester (II, X=Cl, R=Me ; 1.5 g.), and the keto-acid (II, X=Cl, R=H ; 0.4 g.), identical with the migration product, were obtained.

The *diacetyl derivative of the keto-ester* (II, X=Cl, R=Me) crystallised from alcohol in lustrous needles, m.p. 110-12°. (Found: Cl, 10.6. $C_{14}H_{13}O_7Cl$ requires Cl, 10.8 per cent).

The *dibenzoyl derivative* crystallised from alcohol as colorless lustrous plates, m.p. 123°. (Found: Cl, 7.6. $C_{24}H_{17}O_7Cl$ requires Cl, 7.8 per cent).

The *oxime* crystallised from alcohol, m.p. 165° (decomp.).

Hydrolysis of the Ester (II, X=Cl, R=Me) by sodium hydroxide as before gave the keto-acid (II, X=Cl, R=H), crystallised from hot water with a few drops acetic acid as greenish needles, m. p. 232° (decomp.), identical with the acid obtained by the Fries migration.

Decarboxylation of the Acid (II, X=Cl, R=H): *Formation of 2-Acetyl-4-chlororesorcinol* (III, X=Cl).—The keto-acid, when decarboxylated, gave a product which crystallised from dilute alcohol as clusters of bright yellow needles, m.p. 134-35° (0.8 g.). (Found: Cl, 19.1. $C_8H_7O_3Cl$ requires Cl, 19.0 per cent). It gives a green colour with alcoholic ferric chloride and dissolves in cold alkali with a bright yellow colour. It is identical with the hydrolysis product of 8-acetyl-7-hydroxy-6-chloro-4-methylcoumarin (unpublished).

The *Pechmann Condensation of* (III, X=Cl) with ethyl acetoacetate gave 8-acetyl-7-hydroxy-6-chloro-4-methylcoumarin (IV, X=Cl), crystallised from acetic acid in yellow needles, m.p. 201°. (Found : Cl, 14.4. $C_{13}H_9O_4Cl$ requires Cl, 14.1 per cent). It is identical with the migration product of 7-acetoxy-6-chloro-4-methylcoumarin (unpublished).

Fries Migration of 2-Hydroxy-4-O-Acetyl-5-chlorobenzoic Acid (V, X=Cl): *Formation of* (II, X=Cl, R=H)

2-Hydroxy-4-*O*-acetyl-5-chlorobenzoic acid (V, X=Cl) crystallised from benzene in colorless needles, m.p. 136°. (Found: Cl, 15.3. $C_9H_7O_5Cl$ requires Cl, 15.4 per cent). It gives a violet colour with alcoholic ferric chloride.

This migration was carried out at different temperatures (140°, 170°) and also in presence of nitrobenzene. In all cases the same acid (II, X=Cl, R=H) was obtained, identified by mixed melting point.

The *methyl ester of the acid* (II, X=Cl, R=H) crystallised from alcohol in slender needles, m.p. 124°, identical with the product obtained before.

The *monoacetyl derivative* crystallised from alcohol in colorless needles, m.p. 154°. (Found: Cl, 12.9. $C_{11}H_9O_6Cl$ requires Cl, 13.0 per cent). It is soluble in alkali with a yellow colour, and gives a red colour with alcoholic ferric chloride.

The *semicarbazone* crystallised from alcohol in needles, m.p. > 275°.

Attempted Fries Migration of Methyl 2:4-Diacetoxy-5-nitrobenzoate and 2-Hydroxy-4-O-Acetyl-5-nitrobenzoic Acid

The *diacetyl derivative* (I, X=NO_2) of methyl 2:4-dihydroxy-5-nitrobenzoate (Parekh and Shah, *J. Univ. Bombay*, 1943, **11A**, Part V, 101-103; cf. Hemmelmayer, *Monatsh*, 1904, **25**, 33) crystallised from methyl alcohol in needles, turning yellow on keeping, m.p. 101°. (Found: C, 48.2; H, 3.98. $C_{12}H_{11}O_8N$ requires C, 48.5; H, 3.70 per cent).

2:4-*Dihydroxy-5-nitrobenzoic acid* was prepared by the hydrolysis of 2:4-dihydroxy-5-nitrobenzoate.

2-*Hydroxy-4-O-acetyl-5-nitrobenzoic acid* (V, X=NO_2) crystallised from water, as pale yellow needles, m.p. 161° (decomp.). (Found: Equiv., 243.2. $C_9H_7O_7N$ requires equiv., 241.0). Hemmelmayer (*loc. cit.*) gives m.p. of the crude product as 150°.

The migration of (I, X=NO_2) and (V, X=NO_2) was attempted under various conditions at 120°, 140° and 170° with and without nitrobenzene. Only the deacetylated product was obtained, no migration taking place.

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AN IMPROVED METHOD FOR THE PREPARATION OF *bis*-2-THIONAPHTHENE-ETHYLENE-INDIGOS

By Sisir Kumar Guha and Jnanendra Nath Chatterjea

Glyoxal sodium bisulphite may be replaced by glyoxal sulphate with greater advantage in respect of yield and period of reaction in the preparation of *bis*-2-thionaphthene-ethylene-indigos. Several members of this series, two of which are new, have been prepared by both the methods and their respective yields compared.

Kalle and Co. (D.R.P. 239916) reported at first the preparation of *bis*-2-thionaphthene-ethylene-indigo in brownish red needles from glyoxal sodium bisulphite and 3-hydroxythionaphthene without specifying any yield. The same vat dye was obtained in beautiful red needles and in quantitative* yield by Friedländer and Risse (*Ber.*, 1914, **47**, 1924) who employed glyoxal itself in place of its bisulphite compound.

Dutta (*Ber.*, 1933, **66**, 1230; 1934, **67**, V, 9, 1324) used glyoxal sodium bisulphite in the preparation of *bis*-1:2-, *bis*-2:1, and *bis*-2:3-naphthathiophene-ethylene-indigos, but the yield of the dyestuffs was not recorded in any case. Guha (this *Journal*, 1935, **12**, 659; 1937, **14**, 709; 1938, **15**, 359; 1944, **21**, 39) used it in the preparation of the four isomeric *bis*-2- (4-, 5-, 6-, 7-methyl)-thionaphthene-ethylene-indigos and also their parent compound in 48-57% yield. Likewise, Guha and Chatterjea (*ibid.*, 1951, **28**, 103) obtained *bis*-2-(7-chloro)thionaphthene-ethylene-indigo in 30% yield. In the present investigation *bis*-2-(5-chloro)- and *bis*-2-(5-bromo)-thionaphthene-ethylene-indigos in 30% and 28% yield have been obtained.

The present investigation was undertaken with a view to ascertaining if the yields and the period of reaction could be increased and decreased by using glyoxal sulphate. It has been found that glyoxal sulphate condenses readily with 3-hydroxythionaphthenes in acetic acid solution in presence of a catalytic amount of hydrochloric acid. The yield of the dyestuff, in each case, is consistently high and the reaction period is also short (Table I). The condensation also proceeds in absence of hydrochloric acid, due probably to the liberation of sulphuric acid *in situ* which catalyses the reaction. In the case of 3-hydroxythionaphthene itself, the yield of the dyestuff is as high as that obtained by the addition of hydrochloric acid (vide experimental).

In the present work, 3-hydroxythionaphthene, its 5-methyl-, 7-methyl-, 5-chloro-, 7-chloro- and 5-bromo- substituted products were used. Table I clearly reveals the advantage of using glyoxal sulphate in place of glyoxal sodium bisulphite in the preparation of *bis*-2-thionaphthene-ethylene-indigos described here.

* The yield quoted, 1.9 g. of the dye from 1.5 g. of 3-hydroxythionaphthene, is more than the theoretical value which is 1.61 g.

The details of the preparation and properties of 5-bromo-3-hydroxythionaphthene utilised in this work were not recorded before although it was used in E.P. 309379 and 313493. Now it has been obtained from *p*-bromophenylthioglycollic acid adopting the method of preparation of 5-methyl-3-hydroxythionaphthene (Dalgliesh and Mann, *J. Chem. Soc.*, 1945, 893) as cyclisation of *p*-bromophenylthioglycollic acid with phosphorus pentoxide gave poor yield.

TABLE I

G=Glyoxal sodium bisulphite. GS=Glyoxal sulphate. T=Thionaphthene-ethylene-indigo. H=3-Hydroxy-thionaphthene.

Compounds.	Constituents.	Time of reaction.	Yield.
bis-2-T	(a) G+H	1½ hrs.	57 %
	(b) GS+H	15 mins.	87, 84
	(c) GS+H (without catalyst)	15 mins.	84
bis-2-(4-Me)-T	G+4-Me-H	1½ hrs.	56
bis-2-(5-Me)-T	(a) G+5-Me-H	1½ hrs	48
	(b) GS+5-Me-H	20 mins.	84
bis-2-(6-Me)-T	G+6-Me-H	1½ hrs.	54
bis-2-(7-Me)-T	(a) G+7-Me-H	1½ hrs.	53
	(b) GS+7-Me-H	15 mins.	85
bis-2-(5-chloro)-T	(a) G+5-chloro-H	2 hrs.	30
	(b) GS+5-chloro-H	15 mins.	84
bis-2-(7-chloro)-T	(a) G+7-chloro-H	1½ hrs.	30
	(b) GS+7-chloro-H	20 mins.	84
bis-2-(5-bromo)-T	(a) G+5-bromo-H	1½ hrs.	28
	(b) GS+5-bromo-H	20 mins.	73

EXPERIMENTAL

5-Bromo-3-hydroxythionaphthene was obtained from *p*-bromophenylthioglycollic acid (m.p. 118°, 7.4 g.), chlorobenzene (30 c.c.), phosphorus trichloride (3.3 c.c.) and anhydrous aluminium chloride (5 g.) according to the process of Dalgleish and Mann (*loc. cit.*). After removing chlorobenzene by steam distillation, the residue was cooled, made alkaline and filtered. The cold solution was acidified slowly; the separated crystalline precipitate of 5-bromo-3-hydroxythionaphthene was collected, washed well with cold water and dried in a vacuum desiccator, yield 4 g., m.p. 102-105°. The super-heated steam-distilled crystalline product (m.p. 107-109°) after crystallisation from petroleum ether (b.p. 60°-80°) was obtained in clusters of colorless needles, m.p. 109-110.5°. It is soluble in acetone, carbon tetrachloride, alcohol, ethyl acetate, dioxane, acetic acid, benzene and tetralin; very sparingly soluble in water; the solution of the substance in cold strong sulphuric acid and in warm dilute sodium hydroxide is light green. Unlike the ordinary hydroxythionaphthenes, it is very resistant to aero-oxidation. (Found: Br, 34.6. C_8H_5OSBr requires Br, 34.9 per cent).

The indigos described below were purified at first by boiling with alcohol in which they were sparingly soluble and finally crystallised from nitrobenzene, washed with alcohol and hot water. All of them melt above 300°.

bis-2-*Thionaphthene-ethylene-indigo*: *Method* (I).—The silky crystalline red dye separated on boiling a mixture of 3-hydroxythionaphthene (0.60 g.), glyoxal sulphate (0.44 g.), glacial acetic acid (25 c.c.) and concentrated hydrochloric acid (0.3 c.c.) for 15 minutes. It crystallised in darkish red needles, yield 0.56 g. (87%) ; 0.54 g. (84%). (Found: C, 66.8; H, 3.3. Calc. for $C_{18}H_{10}O_2S_2$: C, 67.1; H. 3.1 per cent).

Method (II).—The foregoing compound was also obtained from 3-hydroxythionaphthene (0.3 g.) and glyoxal sulphate (0.22 g.) in glacial acetic acid (12 c.c.) solution when heated for 15 minutes, yield 0.27 g. (84%). (Found: C, 67.2; H, 3.3. Calc. for $C_{18}H_{10}O_2S_2$: C, 67.1; H, 3.1 per cent).

bis-2-(5-*Methyl*) *thionaphthene-ethylene-indigo* separated in violet-red crystals (0.88 g., 84%) when a glacial acetic acid (30 c.c.) solution of 5-methyl-3-hydroxythionaphthene (0.98 g.) and glyoxal sulphate (0.69 g.) containing strong hydrochloric acid (1 c.c.) was boiled for 20 minutes. The dye was obtained in long needles which dissolved in nitrozene producing a beautiful violet-red solution. (Found: S, 17 8. Calc. for $C_{20}H_{14}O_2S_2$: S, 18.3 per cent).

bis-2(7-*Methyl*)*thionaphthene-ethylene-indigo* was similarly prepared in violet-red crystals on boiling for 15 minutes a solution of 7-methyl-3-hydroxythionaphthene (0.45 g.) and glyoxal sulphate (0.32 g.) in glacial acetic acid (15 c.c.) with addition of strong hydrochloric acid (0.2 c.c.), yield 0.41 g. (85 %). (Found : S, 17.9. Calc. for $C_{20}H_{14}O_2S_2$: S, 18.3 per cent).

bis-2-(5-*Chloro*)*thionaphthene-ethylene-indigo*: *Method* (I).—It was prepared in the usual way by heating a mixture of glyoxal sodium bisulphite (0.38 g.) in water (10 c.c.) and 5-chloro-3-hydroxythionaphthene (0.5 g.) in alcohol (20 c.c.) in presence of strong hydrochloric acid (3.7 c.c.) for 2 hours on the water bath. The violet-red dye (0.16 g., 30%) crystallised in needles. It is soluble in nitrobenzene and tetralin ; difficultly soluble in pyridine ; sparingly soluble in carbon tetrachloride and acetone. Strong sulphuric acid dissolves it in cold producing a light green colour. It dyes cotton in uniform deep red-violet shade from a deep yellow hydrosulphite vat. (Found: C, 55.2; H, 2.1. $C_{18}H_8O_2S_2Cl_2$ requires C, 55.2; H, 2.0 per cent).

Method (II).—The foregoing compound was also obtained from 5-chloro-3-hydroxythionaphthene (0.37 g.) and glyoxal sulphate (0.22 g.), dissolved in glacial acetic acid (25 c.c.) containing strong hydrochloric acid (0.3 c.c.) by boiling for 15 minutes. The fine long needle-shaped violet-red dye (0.33 g., 84%) resembles the substance obtained by method (I) in properties. (Found : C, 54.9 ; H, 2.0. $C_{18}H_8O_2S_2Cl_2$ requires C, 55.2 ; H, 2.0 per cent).

bis-2-(7-*Chloro*) *thionaphthene-ethylene-indigo* was similarly prepared from 7-chloro-3-hydroxythionaphthene (0.74 g.) and glyoxal sulphate (0.44 g.) in glacial acetic acid (25 c.c.) and strong hydrochloric acid (1 c.c.) by boiling for 20 minutes. The dye (0.66 g., 84%) crystallised in violet-red needles. (Found: Cl, 18.5. Calc. for $C_{18}H_8O_2S_2Cl_2$: Cl, 18.2 per cent).

bis-2-(5-*Bromo*)*thionaphthene-ethylene-indigo*: *Method* (I).—The dye (0.4 g., 28%) separated on heating a mixture of 5-bromo-3-hydroxythionaphthene (1.374 g.), dissolved in alcohol (55 c.c.) and glyoxal sodium bisulphite (0.852 g.) in water (15 c.c.) containing

concentrated hydrochloric acid (20 c.c.) for 1½ hours. It crystallised in violet-red needles. (Found : C, 44·5; H, 1.9. $C_{18}H_8O_2S_2Br_2$ requires C, 45.0; H, 1.7 per cent).

Method (II).—The same substance also separated when 5-bromo-3-hydroxythionaphthene (0.46 g.) was condensed with glyoxal sulphate (0.23 g.) in glacial acetic acid (25 c.c.) solution with the addition of strong hydrochloric acid (0.5 c.c.) by heating for 20 minutes. The violet-red crystalline dye (0.35 g., 73%) developed a deep red-violet shade on cotton notwithstanding the slow oxidation of the deep yellow hydrosulphite vat. This compound resembles the corresponding 5-chloro compound in solubility. (Found : C, 44.6; H, 1.9. $C_{18}H_8O_2S_2Br_2$ requires C, 45.0; H, 1.7 per cent).

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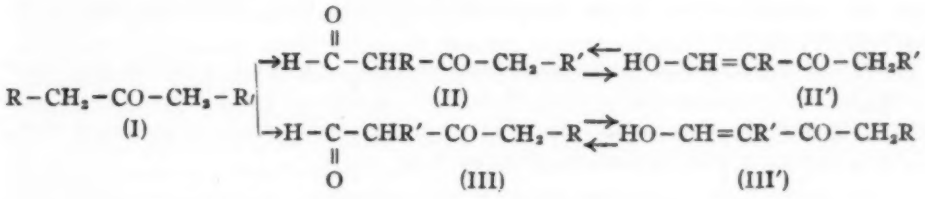
DETERMINATION OF STRUCTURES OF HYDROXYMETHYLENE KETONES THROUGH OXIDATIVE FISSION

By M. M. Bokadia and S. S. Deshapande

Structures of hydroxymethylene ketones are determined by their oxidative fission and identifying the acids formed. Preparations of hydroxymethylene methyl-*n*-amyl ketone and its derivatives are described.

By the action of ethyl formate in presence of sodium on the unsymmetrical ketone (I) two isomeric formylketones (II) and (III) should theoretically be formed which in their enol forms will appear as hydroxymethylene ketones (II′) and (III′) respectively.



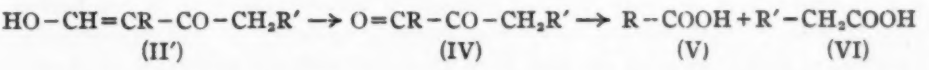
Generally, however, only one form is obtained whose structure could be arrived at by one of the following methods:

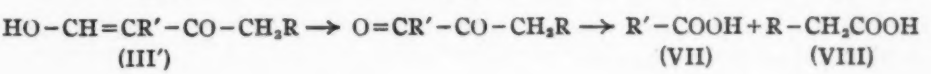
(*i*). Cyclisation with cyanoacetamide, followed by hydrolysis, decarboxylation, reduction and identification of the resulting substituted pyridine (Joshi, Kaushal and Deshapande, this *Journal*, 1941, **18**, 479).

(*ii*). When R′=H, and the structure is (III) or (III′), the ketone undergoes self-condensation and its titre against alkali falls with time (Joshi *et al.*, *loc. cit.*).

The defect of the first method is that in some cases the resulting substituted pyridine may not be identifiable as it might not have been previously synthesised. With the second method it is found that when R′=H, and R is a higher alkyl group, the ketone shows no tendency for self-condensation (Benary, Meyer and Charisius, *Ber.*, 1926, **59**, 108).

An easier and convenient method would be to identify the products of oxidative fission of the hydroxymethylene ketone. The oxidant may attack the ethylenic bond of the hydroxymethylene ketone (II′) producing the 1:2-diketone (IV), which on further oxidation would give a mixture of acids (V) and (VI). The ketone (III′) would similarly give a mixture of acids (VII) and (VIII).





The forms supposed to have been oxidised are the hydroxymethylene forms (II′) or (III′). If the aldehyde forms (II) or (III) also take part in the oxidation, they should yield the corresponding β-ketonic acids which on decarboxylation should yield the original ketone.

$$H-\overset{O}{\overset{\|}{C}}-CHR-CO-CH_2R' \rightarrow HOOC-CHR-CO-CH_2R' \rightarrow R-CH_2-CO-CH_2R'$$

$$H-\overset{O}{\overset{\|}{C}}-CHR'-CO-CH_2R \rightarrow HOOC-CHR'-CO-CH_2R \rightarrow R'-CH_2-CO-CH_2-R$$

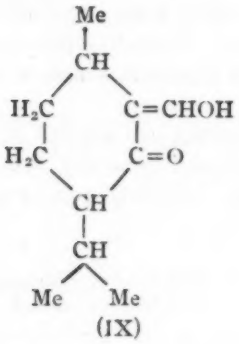
Since in no case did we get a β-ketonic acid or the original (unformylated) ketone, it appears that the form which is oxidised is entirely the hydroxymethylene form (II′) or (III′). Further oxidation of the original ketone (I) should give a mixture of two acids. As on thoroughly examining the oxidation of formylmethylethyl ketone we have found acetic acid as the sole product of reaction, it follows that in the process of oxidation the original ketone is not formed, and hence, the form which is oxidised is the hydroxymethylene form.

By the application of the oxidative fission method we have arrived at the structures of hydroxymethylene ketones derived from some unsymmetrical ketones. These are shown in the following table. As will be seen these structures are in agreement with those arrived at by other workers by other methods.

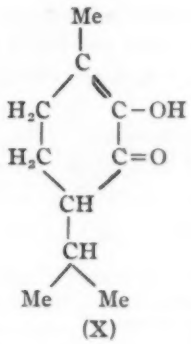
TABLE I

	Ketones.	R and R′.	Products of oxidation.	Structure.	Reference.
(1)	Hydroxymethylene methylethyl ketone	R = Me R′ = H	Acetic acid	(II′)	Diel and Ilberg (*Ber.*, 1916, **49**, 158); Joshi, Kaushal & Deshapande (*loc. cit.*)
(2)	Hydroxymethylene methyl-*n*-propyl ketone.	R = Et R′ = H	*n*-Butyric acid	(III′)	Benary, Meyer and Charisius (*loc. cit.*)
(3)	Hydroxymethylene methyl-*n*-amyl ketone	R = Bu R′ = H	*n*-Caproic acid	(III′)	Synthesised by the present authors.
(4)	Hydroxymethylene bromoacetone.	R = Br R′ = H	Acetic acid	(II′)	Mahala and Deshapande (unpublished work)
(5)	Hydroxymethylene ω-bromoacetophenone	R = Br $CH_2R' = C_6H_5$	Benzoic acid	(II′)	Gupta, Agarwal and Deshapande (this *Journal*, 1949, **26**, 55).

By the action of ozone on hydroxymethylene menthone (IX) Semmler and Makenzie (*Ber.*, 1906, **39**, 1170) obtained diosphenol (X). We oxidised hydroxymethylene menthone with chromic acid in sulphuric acid and obtained a tricarboxylic acid of composition $C_7H_{13}(COOH)_3$. As the opening of the ring through oxidation of hydroxymethylene menthone or diosphenol could not give more than two carboxyl groups, it is obvious that the third carboxyl group has come from one of the two side chains. The structure of this acid is under investigation.



(IX)



(X)

EXPERIMENTAL

The oxidising agent used was Kiliani's dichromate-sulphuric acid mixture (*Ber.*, 1901, **34**, 3564). A mixture of the hydroxymethylene ketone and the oxidant was kept at room temperature with occasional shaking for a number of days for completion of the reaction. The products were extracted with a large volume of ether, the extract washed with a little water, dried over anhydrous sodium sulphate and the solvent removed. The liquid acids were purified by distillation and identified by their boiling points, equivalent weights and melting points of their anilides. The solid acid was purified by crystallisation and identified by its melting point and equivalent weight.

(1). *Hydroxymethylene-methylethyl Ketone.*—The whole of the acid obtained distilled practically at 118° and there was no higher fraction indicating the absence of propionic acid. (Found: Equiv., 60.9; anilide m.p. 114°; acetic acid, b.p. 118°; equiv., 60; anilide m.p. 115°, mixed m.p. with an authentic sample of acetanilide, 114°).

(2). *Hydroxymethylene-methyl-n-propyl Ketone.*—The whole of the liquid distilled at 160°. (Found: Equiv., 89.2; anilide m.p. 90°; *n*-butyric acid, b.p. 162°; equiv., 88; anilide m.p. 90°, mixed m.p. with a genuine sample of anilide of *n*-butyric acid, 90°).

(3). *Hydroxymethylene-methyl-n-amyl ketone* was prepared in the usual manner from methyl-*n*-amyl ketone, which in turn was obtained from ethyl *n*-butylacetoacetate by ketonic hydrolysis (Johnson and Huger, Org. Synthesis, 1927, Vol. 7, p. 60). The hydroxymethylene ketone is a pale yellow liquid (b.p. 77°/25 mm.) which on standing becomes red. (Found: C, 68.01; H, 10.5. $C_8H_{14}O_2$ requires C, 67.6; H, 9.9 per cent). It forms a chelate copper salt which crystallises from benzene in plates and melts at 130°. (Found: Cu, 18.1. $C_{16}H_{26}O_4Cu$ requires Cu, 18.4 per cent). *Phenylhydrazone*, m.p. 113°; *semicarbazone*, m.p. 204° (Found: N, 33.5. $C_{10}H_{20}O_2N_6$ requires N, 32.8 per cent). It is therefore a disemicarbazone.

Oxidation of the hydroxymethylene ketone gave an acid, boiling at 203°-205°. (Found: Equiv., 113.4; anilide m.p. 93°; *n*-caproic acid, b.p. 205°, equiv., 116; anilide m.p. 95°).

(4). *Hydroxymethylene-bromoacetone* gave a bromine-free aliphatic acid, b.p. 118°. (Found: Equiv., 62.5; anilide m.p. 113°; acetic acid, b.p. 118°; equiv., 60; anilide m.p. 115°).

(5). *Hydroxymethylene-ω-bromoacetophenone* gave a solid acid which could be crystallised from boiling water and which melted at 120°. (Found: Equiv., 122; benzoic acid, m.p. 121 ; equiv., 122, mixed melting point with a genuine sample of benzoic acid, 120°).

Hydroxymethylene-menthone.—The oxidation product was purified by dissolving in cold caustic soda and acidifying. The acid, crystallised from dry benzene, melted at 115°. [Found: Equiv., 80.7; C, 51.0; H, 7.2. $C_7H_{13}(COOH)_3$ requires equiv., 77.3; C, 51.7; H, 6.9 per cent].

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CONDENSATION OF AROMATIC ALDEHYDES WITH MALON-1:3:4-XYLIDIC ACID. PART I. WITH BENZALDEHYDE, *m*-METHYL- AND *p*-METHYLBENZALDEHYDES

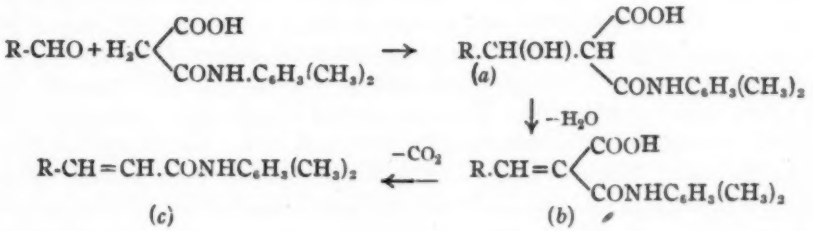
By P. I. Ittyerah and P. T. Chellappa

Malon-1:3:4-xylidic acid was prepared and condensed with benzaldehyde, *m*-methyl- and *p*-methylbenzaldehydes. The condensations were carried out both in the presence as well as in the absence of condensing agents, viz., glacial acetic acid, pyridine and piperidine. A trace of either pyridine or piperidine was found to be a good catalyst in these reactions. With each aldehyde two products were obtained : (1) the corresponding benzylidene-malon-1:3:4-xylidic acid and (2) the corresponding cinnam-1:3:4-xylidide.

The experiments were carried out under different conditions of temperature and time and also both in the presence and in the absence of condensing agents. The observations made in these experiments definitely show that a trace of an organic base like pyridine or piperidine exerts a catalytic influence and makes the reactions quicker with much larger yields of the products.

The present paper deals with the condensation of benzaldehyde, *m*-methyl- and *p*-methylbenzaldehydes with malon-1:3:4-xylidic acid. Malon-1:3:4-xylidic acid was prepared by adapting the method described by Chattaway and Olmsted (*J. Chem. Soc.*, 1910, **97**, 939) for the preparation of malonanilic acid.

In general, it may be stated that all the aldehydes condensed well. A trace of pyridine or piperidine was found to catalyse these condensations. The reaction may be expressed as :



[where R = aryl radical ($C_6H_5^-$, or $C_6H_4(CH_3)^-$), in the cases discussed below].

The aldol (*a*) might be taken as the intermediate, though in these condensations it was never isolated. Products (*b*) and (*c*) were quite stable and could be easily isolated. When no condensing agents were used and the reactions were carried out at 100°, the products were of type (*b*). When a trace of either pyridine or piperidine was used, the products were mainly of type (*c*).

Under the conditions tried the best yields were: benzylidene-malon-1:3:4-xylidic acid, 50%; cinnam-1:3:4-xylidide, 89%; *m*-methylbenzylidene-malon-1:3:4-xylidic acid,

42.1%; *m*-methylcinnam-1:3:4-xylidide, 60%; *p*-methylbenzylidene-malon-1:3:4-xylidic acid, 55%; *p*-methylcinnam-1:3:4-xylidide, 63%. Here a comparison may be made of these results with those obtained by Pandya, Narain and Lal (*Proc. Ind. Acad. Sci.*, 1945, **22A**, 400) in the condensation of malonic acid with *m*- and *p*-methylbenzaldehydes. From the results it appears that in these reactions malon-1:3:4-xylidic acid is not so reactive as malonic acid.

EXPERIMENTAL

Preparation of Malon-1:3:4-xylidic Acid.—A mixture of freshly distilled 1:3:4-xylidine (10 g.) and pure diethyl malonate (20 g.) was gently refluxed for 30 minutes. The alcohol formed was allowed to escape. On cooling rectified spirit (50 c c.) was added. The flask was shaken well and kept aside for 10 minutes. Malon-1:3:4-xylidide separated out (5 g.). This was filtered and the filtrate which contained malon-1:3:4-xylidate was taken. To the filtrate 50 c.c. of a 20% aqueous solution of sodium carbonate was added and then steam was blown through it for 30 minutes. On cooling the flask there was a slight turbidity due to the separation of a small quantity of malon-1:3:4-xylidide. This was filtered off and to the filtrate strong hydrochloric acid was added till the solution was distinctly acidic. A white crystalline precipitate separated out which was filtered and recrystallised from dilute alcohol. After drying, the crystals weighed 12 g. and melted with decomposition at 156°. (Found : Equiv., 206.4 ; N, 6.84. $C_{11}H_{13}O_3N$ requires equiv., 207 ; N, 6.76 per cent). The acid gave a silver salt. (Found: Ag, 34.06. $C_{11}H_{12}O_3NAg$ requires Ag, 34.39 per cent).

Condensation of Benzaldehyde with Malon-1:3:4-xylidic Acid : Formation of Benzylidene-malon-1:3:4-xylidic Acid.—Benzaldehyde (1 g.) and malon-1:3:4-xylidic acid (2 g.) (1:1 mol.) were mixed and heated at 100° for 4 hours. The light yellow solid left was treated with 20 c.c. of a saturated solution of sodium bicarbonate. Most of the product reacted with the alkali and went in solution. The oily drops left were found to be unreacted benzaldehyde. This was removed by extraction with ether. The alkali extract was acidified with concentrated hydrochloric acid. A white crystalline precipitate was obtained. This after purification by recrystallisation from alcohol weighed 0.6 g., m.p. 208° (decomp.). This was identified to be benzylidene-malon-1:3:4-xylidic acid. [Found: N, 4.36. $C_{18}H_{17}O_3N$ requires N, 4.72 per cent. Found (Silver salt) : Ag, 26.67. $C_{18}H_{16}O_3NAg$ requires Ag, 26.86 per cent]. Molecular wight of this acid was determined by titration with standard alkali. (Found : M.W., 295.5. $C_{18}H_{17}O_3N$ requires M.W., 295). Yield of this acid as calculated on the basis of the amount of benzaldehyde used was 21.4%. The yield rose to 50% by prolonging the period of heating to 6 hours, and 9 hours' heating afforded 43% yield (also 17% of cinnam-1:3:4-xylidide).

When the temperature was maintained at 105°-110° for 6 hours, there was increased decarboxylation and both benzylidene-malon-1:3:4-xylidic acid (15%) and cinnam-1:3:4-xylidide (40%) were obtained.

Cinnam-1:3:4-*xylidide*.—Benzaldehyde (1 g.), malon-1:3:4-xylidic acid (2 g.) and 0.1 c.c. pyridine were mixed and heated at 100° for 4 hours. There was a brisk evolution of carbon dioxide. The yellow solid mass obtained was extracted in the usual manner when 0.8 g. of an unsaturated non-acidic substance was obtained. This after recrystallisation from alcohol melted at 181°. On analysis it was found to be cinnam-1:3:4-xylidide. (Found: N, 5.48. $C_{17}H_{17}ON$ requires N, 5.57 per cent).

Heating at 100° for 9 hours or 4 hours' heating with a trace of piperidine in place of pyridine also gave 89% yield. But the yield could not be improved by prolonging the time of heating as the contents of the flask turned dark due to the formation of a resinous matter.

With Glacial Acetic Acid.—On heating together an equimolecular mixture of benzaldehyde, malon-1:3:4-xylidic acid and glacial acetic acid for 4 hours at 100° and then extracting the products in the usual manner, 43% yield of benzylidene-malon-1:3.4-xylidic acid was obtained. No cinnam-1:3:4-xylidide was formed.

Condensation of Malon-1:3:4-*xylidic Acid with* m-*Methylbenzaldehyde*: *Formation of* m-*Methylbenzylidene-malon*-1:3:4-*xylidic Acid*.—On heating together of *m*-methylbenzaldehyde (1.2 g.) and malon-1:3:4-xylidic acid (2 g.) at 100° for 6 hours and then extracting the pale yellow product in the usual manner, 1.3 g. (42.1%) of *m*-methylbenzylidene-malon-1:3:4-xylidic acid was obtained. It was recrystallised from alcohol as colorless needles, m.p. 198° (decomp.). (Found: Equiv., 308.5; N, 4.83. $C_{19}H_{19}O_3N$ requires equiv., 309; N, 4.53 per cent). The silver salt of this acid was prepared and analysed. (Found: Ag, 26.3. $C_{19}H_{18}O_3NAg$ requires Ag, 25.96 per cent).

Heating for 9 hours gave 42.1% yield, but a small quantity (20.2 %) of *m*-methylcinnam-1:3:4-xylidide was also formed.

Formation of m-*Methylcinnam*-1:3:4-*xylidide*.—Benzaldehyde (1.2 g.), malon-1:3:4-xylidic acid (2 g.) and 0.1 c.c. pyridine were mixed and heated at 100° for 7 hours. The mixture first melted to a brown liquid but soon set to a solid. There was a vigorous evolution of carbon dioxide. On extracting the product, an unsaturated, pale yellow, solid substance was obtained. This was recrystallised from alcohol as white needles, m.p. 194°, yield 1.4 g. (53%). (Found: N, 5.13. $C_{18}H_{19}ON$ requires N, 5.28 per cent).

The yield rose to 60% when a trace of piperidine was used in place of pyridine.

Condensation of Malon-1:3:4 *xylidic Acid with* p-*Methylbenzaldehyde* : *Formation of* p-*Methylbenzylidene-malon*-1:3:4-*xylidic Acid*.—*p*-Methylbenzylidene-malon-1:3:4-xylidic acid was obtained in 1.7 g. (55 %) yield when a mixture of 1.2 g. of *p*-methylbenzaldehyde and 2 g. of malon-1:3:4-xylidic acid was heated at 100° for 6 hours. This was recrystallised from alcohol, m.p. 215° (decomp.). (Found: N, 4.69. $C_{19}H_{19}O_3N$ requires N, 4.53 per cent). The silver salt was prepared in the usual manner. (Found: Ag, 26.42. $C_{19}H_{18}O_3NAg$ requires Ag, 25.96 per cent).

Formation of p-*Methylcinnam*-1:3:4-*xylidide*.—An unsaturated non-acid product (1.5 g.), identified to be *p*-methylcinnam-1:3:4-xylidide, was obtained when 1.2 g. of *p*-methylbenzaldehyde, 2 g. of malon-1:3:4-xylidic acid and 0.1 c.c. of pyridine were

heated together at 100° for 7 hours. It was recrystallised from alcohol, m.p. 201°, yield 56.9 %. (Found : N, 5.1. $C_{18}H_{19}ON$ requires N, 5.2 per cent). A small quantity of *p*-methylbenzylidene-malon-1:3:4-xylidic acid (0.4 g.) was also obtained in this experiment.

Under similar conditions when a trace of piperidine was used in place of pyridine a 63% yield of *p*-methylcinnam-1:3:4-xylidide was obtained.

The authors wish to record their gratefulness to Prof. K. C. Pandya for taking keen interest in the work.

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CHEMICAL EXAMINATION OF *IPOMOEA MURICATA* SEEDS. PART IV

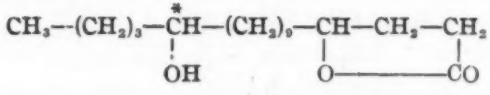
By A. L. Misra and J. D. Tewari

The glucosidic bodies, obtained from *Ipomoea muricata* seeds, tentatively named as Muricatin-A and Muricatin-B, have been further investigated. Oxidation of the former with concentrated nitric acid furnishes (1) butyric and valeric acids ; (2) an acid, $C_{10}H_{18}O_4$ (m.p. 104°), isomeric with sebacic acid ; (3) an acid, $C_{14}H_{24}O_4$ (m p. 63-64°) and (4) oxalic acid. On fusion with caustic potash the former yields formic and butyric acids as steam-volatile products and an acid of m p. 104-105°, akin to the one obtained in its oxidation. Muricatin-B related to A as its ethyl ester has been further degraded to its sugar-free component (aglucone, $C_{18}H_{34}O_3$) obtained from it by acid hydrolysis with 5% sulphuric acid.

The communication deals with the nature of the glucosidic body, its probable constitution by analytical methods which provide a clue to the constitution of the glucosidic bodies present in the seeds.

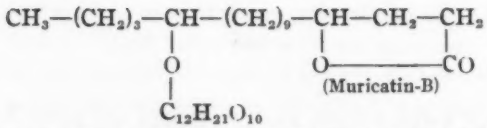
In continuation of our work in the previous parts (this *Journal*, 1951, **28**, 371 ; 1952, **29**, 60, 430) we have obtained a fixed oil, an enzyme, a lipoid, an organic acid and a glucosidic body, tentatively termed as Muricatin-A. The oxidation of this glucosidic body yields butyric and valeric acids, an acid corresponding to $C_{10}H_{18}O_4$ (m.p. 104°), isomeric with sebacic acid, an acid corresponding to $C_{14}H_{24}O_4$ (m.p. 63-64°) and oxalic acid. These acids have been worked up in detail. The acid corresponding to $C_{10}H_{18}O_4$ (m.p. 104-105°) is also obtained along with formic and butyric acids as steam-volatile products in the potash fusion of the glucosidic body. The alkaline hydrolysis of muricatin-A converts it into another glucosidic body, muricatin-B, to which the former is related as its ethyl ester. The elucidation of the structure of these glucosidic bodies presents difficulties, and hence, their probable nature has been arrived at by a study of the degradation products obtained by oxidation, reduction, acetylation etc., of *dextro*-rotatory aglucone $C_{18}H_{34}O_3$, the sugar-free component of muricatin-B from which it is derived by acid hydrolysis with 5% sulphuric acid.

From reactions described in detail in the experimental section, the following structure has been proposed for the aglucone obtained by the acid hydrolysis of muricatin-B.



[Aglucone of muricatin-B]

The marked carbon atom is asymmetric and is responsible for the optical activity of the molecule. It appears that the two molecules of the reducing sugar are linked to the hydroxy group of the marked carbon atom and the linking appears to be of a disaccharide type; hence the probable formula for muricatin-B and A are :

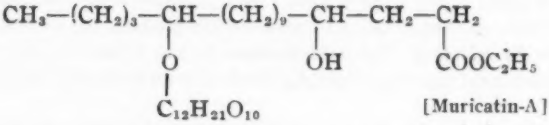


(Muricatin-B)

or $C_{30}H_{54}O_{13} + 2H_2O \longrightarrow 2C_6H_{12}O_6 + C_{18}H_{34}O_3$

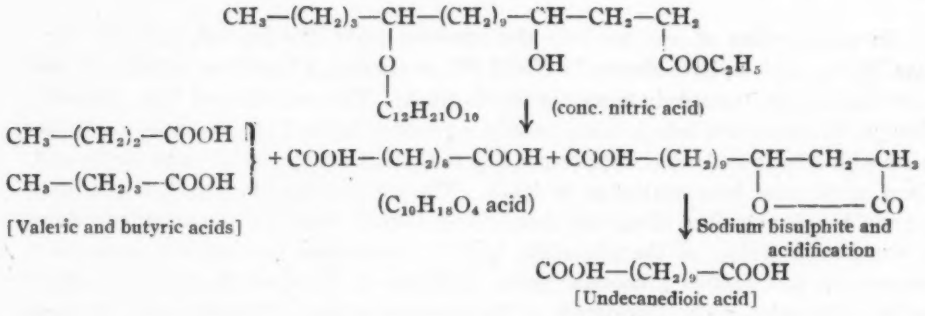
[Aglucone]

Muricatin-A, obtained by the alcoholic extraction of the seeds or by the esterification of muricatin-B, has been assigned the following structure in which it is shown to be related to the latter as its ethyl ester.



[Muricatin-A]

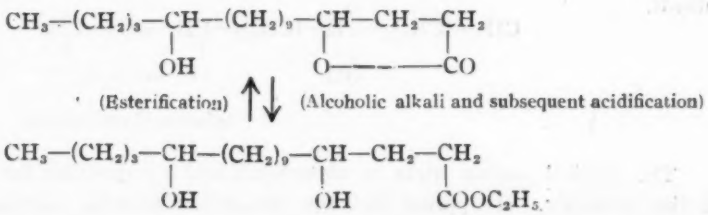
The oxidation of muricatin-A wtth concentrated nitric acid proceeds as follows:



[Valeric and butyric acids]

[Undecanedioic acid]

The lactonic acid, $C_{14}H_{24}O_4$ (m.p. 63-64°) is assigned the proposed structure on account of its properties, reactions and close similarity in behaviour with the general properties of γ-hydroxy-acids and γ-lactones (*Ber.*, 1891, **24**, 1237). The waxy aglucone $C_{18}H_{34}O_3$ (m.p. 63-64°) having the lactonic structure can be readily converted into its corresponding hydroxy-acid ester by refluxing with absolute alcohol and a few drops of concentrated sulphuric acid. The reversibility of these compounds is as shown below :



The above hydroxy-acid ester of the agluconic body on oxidation with chromic acid in glacial acetic acid gave a product of m.p. 76-77° corresponding to $C_{20}H_{36}O_4$

which on further oxidation with nitric acid gave undecanedioic acid, $C_{11}H_{20}O_4$ (m.p. 108°-109°) and butyric acid, confirming the fact that in the intermediate oxidation product the $-(CH_2)_9-$ group is shielded on either side by two easily breakable -CO- linkages.

$$CH_3-(CH_2)_3-\underset{\underset{OH}{|}}{CH}-(CH_2)_9-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2-COOC_2H_5 \xrightarrow{2O}$$

$$CH_3-(CH_2)_3-CO-(CH_2)_9-CO-CH_2-CH_2-COOC_2H_5 \xrightarrow{O}$$

$$CH_3-(CH_2)_2-COOH + COOH-(CH_2)_9-COOH$$

[Butyric acid] [Undecanedioic acid]

The reduction of the aglucone with hydriodic acid and red phosphorus yields a syrupy iodinated derivative which on further reduction with amalgamated zinc and hydrochloric acid affords stearic acid, signifying the length of the carbon chain as that of 18 carbon atoms.

It is interesting to mention that *Ipomoea hederacea* seeds belonging to the same Natural Order as the seeds under investigation (Asahina and Yaoi, *J. Pharm. Soc., Japan*, 1925, No. 523, 5) have as their active principle described by Dymock (*Pharmacographia Indica*, Vol. II, p. 530, 1891) a pale yellow resin existing to the extent of 8% on the weight of the seeds. The properties of the muricatin-B in the present investigation fit in well with those of the active principle of *Ipomoea hederacea*, and hence, it may rightly be claimed to have the properties of the drug. The cathartic action of the seeds may be due to the fixed oil present in them.

EXPERIMENTAL

Oxidation of Muricatin-A.—To muricatin-A (15 g.), made into a paste with a little water, about 150 g. of nitric acid (*d* 1.54) was added when a vigorous reaction ensued with the evolution of nitrous oxide fumes (Power and Rogerson, *J. Amer. Chem. Soc.*, 1910, **32**, 80; *J. Chem. Soc.*, 1912, **101**, 398). Towards the end of the reaction more nitric acid was added to ensure complete oxidation and the contents refluxed over a water-bath for over 5 hours when evolution of brown fumes ceased. The mixture was steam-distilled to recover volatile products. The steam distillate on being shaken with ether gave a liquid smelling strongly of butyric and valeric acids.

From the aqueous liquid remaining in the flask after steam-distillation, colorless flakes separated out at the bottom on cooling and a pale yellow, waxy substance remained floating on the surface. These two products were separated and purified. The mother-liquor on concentration yielded another substance, identified to be oxalic acid.

Steam-volatile Products of Oxidation.—The steam-distillate on being extracted with ether and subsequent evaporation of the solvent left an oily liquid which formed a silver salt. The percentage of silver in it falls between those of the silver salts of butyric and valeric acids pointing thereby that these two acids are steam-volatile products formed in the oxidation of muricatin-A.

Other Products of Oxidation.—The colorless flakes, as mentioned above, were filtered, washed thoroughly with cold water till perfectly white, and redissolved in boiling water (animal charcoal) and filtered. The filtrate on cooling deposited colorless crystals, m.p. 104°. The crystals dissolve readily in alcohol but are only sparingly soluble in cold water. In aqueous solutions of sodium carbonate or caustic soda, they dissolve readily forming sodium salts. The neutral sodium salt gives a marked precipitate with lead acetate or silver nitrate and a buff coloured precipitate with ferric chloride. [Found : C, 59.04 ; H, 8.87 ; M. W. 206 (silver salt). $C_{10}H_{18}O_4$ requires C, 59.40 ; H, 8.91 per cent. M.W., 202].

The *toluidide* and *anilide* of the acid prepared by usual methods melt at 190-92°, 192-93°, respectively (those of sebacic acid melt at 201° and 198° respectively).

This acid, though isomeric with sebacic acid, differs from it in m.p. It appears to be identical with ipomic acid obtained by oxidation of Convolvulin by nitric acid (Höhnel, *Arch. Pharm.*, 1896, **234**, 679 ; *Amer. Chem. Pharm.*, 1852, **83**, 143; 1885, **95**, 160).

Neison and Bayne (*J. Chem. Soc.*, 1874, **27**, 729) established the identity of Ipomic acid as sebacic acid contaminated with its lower homologue. After repeated crystallisations the acid under the present investigation too melted at 126-27° and its toluidide and anilide in the neighbourhood of those of sebacic acid. A solution of the acid in absolute alcohol was devoid of any optical activity.

Isolation and Properties of the waxy acid.—It is a cream coloured waxy solid, m.p. 63-64°, which easily dissolves in ether, alcohol, acetone but is insoluble in water. When heated in water it melts forming a dark coloured brown oil settling at the bottom of the flask. It dissolves in solutions of caustic soda or sodium carbonate very slowly giving a gelatinous precipitate of the sodium salt, which, however, dissolves in water giving an opalescent solution. From this solution after neutralising the excess of alkali by dilute nitric acid and excess nitric acid by ammonia and removing the excess of ammonia by boiling, a colorless silver or lead salt can be prepared by adding silver nitrate or lead acetate. Ferric chloride gives a buff coloured precipitate with neutral sodium salt. Determination of its molecular weight by alkali titration presented difficulties. Attempts to find the neutralisation value of the acid and its mean molecular weight by alkali titration did not give satisfactory results. Very low values of mean molecular weight (90.76, 77.25) were obtained. On adding the waxy acid to a strong solution of sodium bisulphite, the acid slowly went into solution evolving sulphur dioxide and precipitation of its gelatinous sodium salt which on being boiled with dilute hydrochloric acid (excess) slowly deposited colorless shining needles of undecanedioic acid, m.p. 108-109° (Peyer and Rosenthal, *Apoth. Ztg.*, 1929, **44**, 1329 ; *J. Amer. Chem. Soc.*, 1928, **50**, 1749). [Found : C, 65.07 ; H. 9 63 ; M.W., 260.3 (silver salt). $C_{14}H_{24}O_4$ requires C, 65.66 ; H, 9.37 per cent. M.W., 256].

Undecanedioic acid was obtained in small yields. [Found : C, 60.8 ; H, 8.9 ; M. W. (Rast), 220. Calc. for $C_{11}H_{20}O_4$: C, 61.1 ; H, 9.2 per cent. M.W., 216].

The anilide of the acid melts at 154-55° (lit. m.p. 156°).

Oxalic Acid.—The mother-liquor after separation of the above products on concentration yielded beautiful plates of oxalic acid (analysed), m.p. 100-101°.

Potash Fusion of Muricatin-A.—Muricatin-A (2.5 g.) and KOH (10 g.) were made into a paste with a little water and heated with constant stirring to 140°-150°. Temperature was raised to 250° towards the completion of the reaction when all the frothing subsided. The mass was then cooled, transferred to a beaker and filtered and the filtrate steam-distilled till about 300-400 c.c. of the distillate was recovered. This on being extracted with ether gave an oily liquid, identified to be a mixture of formic acid and butyric acid with other intermediate fatty acids. The liquid remaining in the distilling flask after the separation of the brownish gummy matter was concentrated over a water-bath and shaken with ether, when from the ethereal layer an oily liquid was obtained which set to a solid on keeping for sometime. This was taken up in boiling water and adhering oily matter removed by filtration. The clear yellow liquid was boiled with animal charcoal and filtered. The filtrate deposited crystals of an acid of m.p. 104-105°, corresponding to $C_{10}H_{18}O_4$ and akin to the one obtained in the oxidation of muricatin A by concentrated nitric acid.

Acid Hydrolysis of Muricatin-B.—Muricatin-B (10 g.) was refluxed with 250 c.c. of 5% sulphuric acid on a wate-rbath for 4 to 5 hours. With the progress of hydrolysis the resin went into solution and a waxy mass remaining molten in the hot liquid began to float at the bottom of the flask. After completion of the hydrolysis, the contents were shaken with ether, the ethereal layer dried over anhydrous sodium sulphate and filtered. The filtrate on slow removal of ether yielded star-shaped, pale yellow, waxy crystals of the aglucone, $C_{14}H_{24}O_3$, m.p. 54-55°.

The aqueous solution resulting from the acid hydrolysis of muricatin-B was subsequently treated with baryta, filtered and the filtrate evaporated under reduced pressure to a syrupy consistency. This mass yielded with phenylhydrazine a yellow crystalline osazone, m.p. 200-202°.

Properties of the Aglucone.—The pale yellow, waxy aglucone is soluble in alkalies on warming with a pale yellow colour and is reprecipitated on acidification. Dilute sodium carbonate dissolves it on warming to give a yellow solution. It does not give any characteristic colour with aqueous or alcoholic ferric chloride nor does it decolorise bromine solution in chloroform. It does not reduce Tollen's reagent. With concentrated sulphuric acid dissolution occurs forming an intense red colour. With warm concentrated nitric acid brown fumes begin to come out and the reaction becomes vigorous due to oxidation. With warm potassium permanganate, decolorisation occurs and no precipitate is obtained with lead acetate. (Found: C, 72.19; H, 10.83; M.W., 295, 296 3. $C_{14}H_{24}O_3$ requires C, 72.45; H, 11.40 per cent. M.W., 298).

The equivalence of aglucone by alkali titration method agreed well with the one theoretically calculated. In absolute alcohol, the specific rotation $[\alpha]_D^{31} = + 2.232$, pointing out the presence of a centre of asymmetry in the molecule.

The *ethyl ester* of the aglucone, prepared according to the usual method, crystallises in white crystalline flakes, m.p. 35-36°. (Found: C, 70.06; H, 11.22; M.W. 340, 342. $C_{20}H_{40}O_4$ requires C, 69.76; H, 11.62 per cent. M.W., 344).

The *methyl ester* melts at 43-44°. (Found: C, 68.79; H, 11.20; M. W., 332-334. $C_{19}H_{36}O_4$ requires C, 69.09; H, 11.51 per cent. M.W., 330).

Reversibility of the Aglucone and its Ethyl Ester.—The aglucone was converted into its ester by the usual method and the ester taken up in absolute alcohol was refluxed with alcoholic caustic potash solution for 6 hours on a water-bath. After removal of the alcohol the corresponding potassium salt was dissolved in water, acidified with dilute sulphuric acid and extracted with ether. The ethereal liquid after being dried over fused calcium chloride and removal of the solvent left a pale yellow waxy crystalline compound, m.p. 53-55°, identified in every respect to be the original aglucone from which the ester was prepared, establishing the reversibility of the two bodies.

Acetylation of the aglucone was carried out by refluxing the aglucone (0.5 g.) with 10 c.c. of acetic anhydride (pyridine) for over 12 hours. On cooling a soft waxy mass separated which was filtered, washed first with dilute HCl and then with dilute sodium bicarbonate solution to free the product from the adhering acid. The product, when crystallised from ether, gave a reddish oily liquid which failed to crystallise at room temperature. (Found: C, 65.57; H, 9.70; M.W., 395.8. $C_{22}H_{40}O_6$ requires C, 66.0; H, 10.0 per cent. M.W., 400).

A known weight of the acetylated product (0.5482 g.) requires 35.5 c.c. of 0.094*N* sodium hydroxide solution, which gave 26.18% as the percentage of acetyl radical in the compound. Taking the molecular weight of the aglucone as 298, the value of the number of acetyl groups, and hence the number of hydroxyl groups in the compound, comes out to be 1.92, or 2.

Oxidation of Ethyl Ester of the Aglucone with Chromic Acid.—To the hot solution of ethyl ester of the aglucone (0.5 g.) taken up in glacial acetic acid, a little more than an equivalent amount of chromic acid (sufficient to oxidise two hydroxyl groups) in a little concentrated sulphuric acid and glacial acetic acid was added dropwise when an instantaneous colour change from yellowish brown to green took place. After the addition of the requisite amount of chromic acid solution, the contents were refluxed on a water-bath for 2 to 3 hours and then poured while hot into ice-cold water. The white gelatinous precipitate separating was filtered, well washed with water to remove adhering chromic sulphate and recrystallised from ether, m.p. 76-77°. (Found: C, 70.84; H, 11.14; M.W., 337, 342. $C_{20}H_{36}O_4$ requires C, 70.59; H, 10.60 per cent. M.W., 340).

Oxidation of the Oxidised Ethyl Ester of the Aglucone with Nitric Acid.—To about 0.3 g. of the oxidised ester in a round-bottomed flask 10 c.c. of nitric acid (*d* 1.54) were added and the contents slightly warmed on a water-bath when brown fumes began to evolve. After moderation of the reaction, the contents were heated on a water-bath for 1-2 hours till the colour of the solution became white. Butyric acid was the steam-volatile product recovered which was confirmed by the formation of its silver salt and the determination of the percentage of silver in it. From the mother-liquor after the addition of a little amount of animal charcoal, boiling, filtering, and concentration of the filtrate, white shining needle-shaped crystals separated out on cooling. These were filtered out and recrystallised from boiling water in needles, m.p. 108-110°. It was subsequently confirmed to be undecanedioic acid by combustion data and melting point of its toluidide.

Reduction of the Aglucone.—The reduction of the aglucone (1 g.) was carried in a Carius tube with hydriodic acid (57%, 5 g.) and red phosphorus (2 g. approx.) at 120°-130° for over 6 hours. After cooling, the contents of the tube were shaken with ether, the clear ethereal liquid well washed with distilled water till washings did not give any precipitate with silver nitrate. The ethereal liquid was dried over anhydrous sodium sulphate and filtered. The filtrate after removal of the solvent left a reddish brown syrupy liquid containing iodine. The syrupy liquid was taken up in hydrochloric acid (1 vol. conc. acid and 8 vols. of water) and to it freshly prepared amalgamated zinc added and heated under reflux. The contents were then drained off from the zinc, and when cool, extracted with ether, the ethereal layer being well washed with water, dried and after removal of the solvent left a crude, yellowish white, waxy compound. This compound reacts acid to litmus in alcoholic solution and is an acid. It was purified through the preparation of its lead salt (m.p. 114-115°) and reprecipitation by hydrochloric acid in colorless crystals, m.p. 68-69.5° (M.W., 278, 280). It was identified to be stearic acid. In one of the reductions of the aglucone with hydroiodic acid and red phosphorus in which the temperature went up to 230°-240°, an iodine-free product having kerosene oil smell was obtained which, when distilled, gave a yellowish brown liquid having an intense greenish fluorescence in ethereal solution and which decolorised an ethereal bromine solution. It appears that the long aliphatic chain has cyclised to give a closed-chain compound of naphthene type under the conditions of the experiment.

One of us (A. L. M.) wishes to make a grateful acknowledgement to the Kanta Prasad Research Scholarships Endowment Trust of Uttar Pradesh for the award of a research scholarship which enabled him to take part in this investigation.

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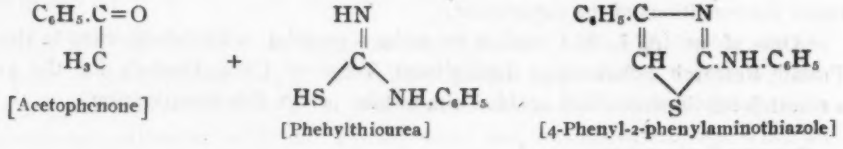
PREPARATION OF N-SUBSTITUTED 2-AMINOTHIAZOLES. PART I. CONDENSATION OF ACETOPHENONE WITH SUBSTITUTED THIOUREAS

By G. N Mahapatra and M. K. Rout

Twelve N-substituted 2-aminothiazoles have been prepared by the condensation of acetophenone with different substituted thioureas in presence of I_2. Their picrates and acetyl derivatives have also been isolated and characterised.

The present investigation deals with the preparation of some N-substituted 2-aminothiazoles. Aminothiazoles were first prepared by Traumann by reacting thiourea with α-haloketone (*Annalen*, 1888, **31**, 249). Dodson and King subsequently demonstrated that ketones reacted with thiourea in presence of halogens to give 4- or 5-substituted 2-aminothiazoles (*J. Amer. Chem. Soc.*, 1945, **67**, 2242). In the present work, this reaction has been examined as a preparative method for N-substituted 2-aminothiazoles by effecting condensation between substituted thioureas and acetophenone in presence of iodine. The formation of thiazoles proceeds according to the following scheme :



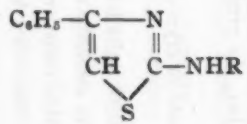
Experimental

The phenyl- and tolylthioureas (Hofmann, *Ber.*, 1868, **1**, 201) were prepared by the action of alcoholic NH_3 on phenyl and tolyl *iso*thiocyanates, obtained by the methods of Dains, Brewster and Olander ("Organic Synthesis," Vol. 1, p. 437). The chlorophenyl-, carboxyphenyl- and naphthyl-thioureas were obtained by the action of ammonium thiocyanate on the hydrochlorides of the corresponding bases (De Clermont, *J. Chem. Soc.*, 1877, **31**, 70).

The experimental procedure adopted for the preparation of the thiazoles is nearly the same in all cases with slight variations and has been illustrated in one particular case (described below).

4-Phenyl-2-phenylaminothiazole.—A mixture containing phenylthiourea (10.8 g., 2 *M*), acetophenone (4 g., 1 *M*.) and iodine (8.2 g., 1 *M*) was heated under reflux for 8 hours on a water-bath and again for another 12 to 16 hours after removal of the condenser. The period of heating influenced the yield of the final product. The crude reaction product, which was coloured due to iodine, was kept for 48 hours in contact with ether (to remove unchanged ketone which otherwise led to a gummy product). Final removal of iodine was effected by treatment with $Na_2S_2O_3$

TABLE I



4-Phenyl-2-R-aminothiazole

R=	M.p.	Approx. yield.	%Nitrogen. Found.	%Nitrogen. Calc.	%Sulphur. Found.	%Sulphur. Calc.	Picrate M.p.	Picrate Approx. yield.	Picrate % Sulphr Found.	Picrate % Sulphr Calc.	Acetyl derivative M.p.	Acetyl derivative Approx yield.	Acetyl derivative % Sulphur. Found.	Acetyl derivative % Sulphur. Calc.
1. Phenyl	75-76°	80%	10.65	11.1	12.24	12.69	182°	90	6.81	6.65	120°	85%	10.65	10.88
2. *o*-Tolyl	126°	88	10.05	10.53	11.8	12.03	212°	92	6.65	6.46	112°	83	10.52	10.39
3. *m*-Tolyl	...	...	8.75*	9.09*	—	—	178°	94	6.12	6.46	133°	82	10.60	10.39
4. *p*-Tolyl	139-40°	80	10.1	10.53	11.95	12.03	186°	88	5.98	6.46	118°	85	10.12	10.39
5. *o*-Chloro-phenyl	72°	25	10.1	9.77	11.48	11.17	128°	90	6.02	6.21	...	...	...	...
6. *m*- ,,	98°	45	10.1	9.77	11.33	11.17	116°	94	6.52	6.21	90°	86	10.01	9.74
7. *p*- ,,	142-44°	45	9.95	9.77	11.52	11.17	190°	90	6.03	6.21	154°	88	9.95	9.74
8. *o*-Carboxy-phenyl	270-72°	45	9.82	9.46	11.20	10.81	120°	93	5.85	6.1	274°	86	9.13	9.47
9. *m*- ,,	260°	40	9.75	9.46	11.09	10.81	221°	92	5.83	6.1	186°	85	9.17	9.47
10. *p*- ,,	252°	50	9.65	9.46	11.27	10.81	216°	90	5.78	6.1	211°	86	9.56	9 47
11. α-Naphthyl	120-22°	60	9.75	9.27	10.82	10.6	206°	90	5.81	6.03	152°	82	9.52	9.3
12. β- ,,	110-11°	58	9.65	9.27	10.85	10.6	204°	87	5 72	6.03	134°	80	9.12	9.3

*refer to acetyl derivative

solution. The nearly colorless resulting product was boiled with water and filtered hot. The residue was treated with conc. NH_4OH to liberate the base and then filtered. The product was crystallised 2 or 3 times from 50% alcohol. In some cases, the residue after boiling with water was gummy. In such cases, longer contacts (for 7 to 8 hours) with conc. NH_4OH or even refluxing with conc. NH_4OH on a water-bath were necessary. The gummy products hardened up after such treatments with one or two exceptions.

In case of compounds Nos. 8, 9, 10 (Table I) the reaction products were soluble in ammonium hydroxide from which the bases separated by acidification with acetic acid. To the filtrate (obtained after acidification and filtration), copper acetate solution was added to isolate the base (which might have passed into the filtrate) as Cu salt, but there was no precipitate.

In case of compound No. 11, the final product was surprisingly found to be gummy. The gummy base was again converted into hydrochloride by addition of HCl and subsequently kept in contact with ether for 48 hours to render it completely free from adhering ketone which was suspected to make the product gummy. The base was freed by adding conc. NH_4OH and evaporating off the ether; it was crystalline. This was also done in another way, e.g., by treating its picrate (which was crystalline) with LiOH and then extracting with ether. After evaporation of the ether, the product was found to be crystalline (cf. Table I).

Both these methods, however, failed to isolate the base in crystalline state in case of compound No. 3 (cf. Table I).

The thiazole bases were acetylated by heating with acetic anhydride in presence of pyridine for about 20 minutes. The picrates were prepared in alcoholic medium.

For a study of any possible relationship between chemical constitution and biological activity, work on the preparation of thiazoles derived from other ketones or ketonic esters and investigation of their biological properties are in progress. Preparation of sulphathiazoles as well as As, Sb and Hg derivatives of these thiazoles has also been undertaken.

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5:6-BENZOQUINALDINIC ACID AS AN ANALYTICAL REAGENT. PART IV. SEPARATION OF COPPER FROM DIFFERENT ELEMENTS

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The reagent 5:6-benzoquinaldinic acid is utilised for the separation of copper from zinc, cobalt, nickel, manganese, silver, mercury, lead, beryllium, iron^{III}, aluminium, chromium^{III}, titanium^{IV}, rare-earths, zirconium, thorium, tin^{IV}, antimony^{III}, bismuth, vanadium, molybdenum, tungsten and uranium^{VI}, by means of p_H control, and where necessary, by complexing agents.

In Part I of this series (Majumdar and Mallick, this *Journal*, 1952, **29**, 255) 5:6-benzoquinaldinic acid was used for the estimation of copper and its separation from calcium, barium, strontium, magnesium, citrate, tartrate, phosphate, arsenate and arsenite. It was observed that copper could be gravimetrically estimated at any p_H above 0.82. The same reagent was further utilised for the estimation of cadmium and its separation from copper (Part II, Majumdar and De, *ibid.*, 1952, **29**, 499) and for the estimation of Zn, Ni, Co and Mn (Part III, *ibid.*, 1953, **30**, 123). The present paper deals with the different conditions under which copper can be separated from elements other than those reported in Part I (*loc. cit.*).

Excepting mercury, zirconium, antimony^{III}, tin^{IV}, titanium^{IV} and rare-earths, practically all the elements are separated from copper only by p_H control.

For the separation from mercury, copper is estimated in ammoniacal solution, while zirconium, titanium, tin, antimony and the rare-earths are kept in solution in presence of tartrate. As copper is precipitated at a p_H as low as 0.82, the separations that are done by simple control of p_H can be extended up to that limit.

Experimental

The reagents and chemicals used are the same as described in previous parts and are of the analytical variety except where specifically mentioned. An 1% solution of sodium benzoquinaldinate (1 g. of the 5:6-benzoquinaldinic acid of m.p. 187° per 100 c.c. of the solution) was used as a precipitant for copper.

Copper, zinc, cobalt, manganese, nickel and alkaline earth solutions were prepared and standardised in the same way as reported in Parts I-III (*loc. cit.*).

Solutions of silver nitrate (E. Merck, Extra Pure), mercuric nitrate (E. Merck, Extra Pure), lead nitrate, beryllium nitrate (B.D.H., L.R.), thorium nitrate (B.D.H., L.R.), zirconium oxychloride, uranyl nitrate (B.D.H., L.R.), ferric chloride, aluminium nitrate (Scherring-Kahlbaum, Pure), chromic sulphate, ammonium vanadate (B.D.H., L.R.), ammonium molybdate, sodium tungstate (B.D.H., L.R.), bismuth nitrate from bismuth subcarbonate (Scherring-Kahlbaum, Pure), antimony trichloride from antimony oxide (Baker), stannic chloride from stannous chloride and chlorine and titanic sulphate from titanium dioxide fused with bisulphate, were prepared and their strengths determined by standard methods.

The rare-earths from Indian monazite sand after separation of thorium were precipitated as oxalates and ignited to the oxide. These oxides (ΣR_2O_3) were dissolved in HCl in presence of a few drops of H_2O_2 and from this solution rare-earth oxalates were reprecipitated, filtered, washed, dried and again ignited to the oxide which was then dissolved in HCl with a few drops of H_2O_2, and the solution made up to a definite volume. From an aliquot portion of the solution the rare-earths were determined as mixed oxides after precipitation with ammonia.

(*a*) *Separation of Copper from Zinc, Cobalt, Nickel and Manganese.*—The procedure for the estimation of copper and its separation from these elements was similar to that reported in Part II of the series (*loc. cit.*). The p_H of the solution was adjusted to 1.10-1.80 in presence of zinc, 1.45-1.92 in presence of cobalt, 1 58-1.98 in presence of nickel and 1.05-1.60 in presence of manganese. From the respective filtrates the elements (zinc, cobalt, nickel, manganese) were determined in the same way as was done in the case of cadmium in the filtrate from copper (cf. Part II, *loc. cit.*). Drying temperatures were 110°-115° for zinc (f=0.1240), manganese (f= 0.1010) and nickel (f=0.1072) and 150°-155° for cobalt (f=0.1172) (cf. Part III, *loc. cit.*). As copper is completely precipitated even at p_H 0.82, the p_H range for separation could be extended to this limit. The interfering elements, as mentioned above, co-precipitated when the p_H of the solution was raised above 1.80, 1.92, 1.98 and 1.60 respectively.

The results for the separations are given in Tables I-IV.

TABLE I

No.	Metals taken.	Sulphuric acid (1*N*).	Reagent solution.	p_H.	Wt. of salts.	Metals found.	Error.
1	Cu 10.77 mg. Zn 10.02	25 c.c.	10. c.c	1.10	90.60 mg. 80.60	10.77 mg. 9.99	Nil −0.03 mg.
2	Cu 5.39 Zn 20.04	,,	5	1.14	45.20 161.80	5.37 20.06	−0.02 +0.02
3	Cu 5.39 Zn 40.08	,,	5	1.12	45.30 322.80	5.39 40.03	Nil −0.05
4	Cu 16.16 Zn 5.01	,,	15	1.12	135.80 40.30	16 15 5.00	−0.01 −0.01
5	Cu 26.93 Zn 5.01	,,	25	1.15	227.00 40.50	26.99 5.02	+0.06 +0.01
6	Cu 5.39 Zn 5.01	15	5	1.40	45.40 40.40	5 40 5.01	+0.01 Nil
7	,,	10	,,	1.62	45.20 40.30	5.37 5.00	−0.02 −0.01
8	,,	6	,,	1.80	45.60 40.10	5.42 4.97	+0.03 −0.04
9	,,	4	,,	1.90	46.40 39.60	5.52 4 91	+0.13 −0.10
	,	3	,,	2.05	48.20 38.00	5.73 4.71	+0.34 −0.30

TABLE II

No.	Metals taken.	Sulphuric acid (1N).	Reagent solution.	p_H.	Wt. of salts.	Metals found.	Error.
1	Cu 8.62 mg. Co 9.12	15 c.c.	8 c.c.	1 48	72.60 mg 78.00	8.63 mg. 9.14	+0.01 mg. +0.02
2	Cu 4.31 Co 18.24	,,	4	1.50	36 20 155 60	4.30 18.24	−0.01 Nil
3	Cu 4.31 Co 34 20	,,	4	1.53	36.30 292.20	4.31 34.30	Nil +0.10
	Cu 16.16 Co 4.56	,,	15	1.45	136.00 38 80	16.17 4.55	+0.01 −0.01
	Cu 26.93 Co 4.56	,,	25	1.50	226.4 38.90	26.92 4.56	−0.01 Nil
6	Cu 5 39 Co 4.56	4	5	1.92	45.50 38.70	5.41 4.54	+0.02 −0.02
7	,,	3	5	2.10	46.00 38.00	5.47 4 45	+0.08 −0.11
8	,,	1	5	2.45	50.10 34.10	5.96 4.00	+0.57 −0.56
9	Cu 5.19 Co 129.2	15	4.8	1.52	43.7 —	5.19 —	Nil —

TABLE III

No.	Metals taken.	Sulphuric acid (1N).	Reagent solution.	p_H.	Wt. of salts.	Metals found.	Error.
1	Cu 10.20 mg. Ni 10.61	10 c c.	9.2 c.c.	1.60	85.7 mg. 99.0	10.19 mg. 10.61	−0.01 mg. Nil
2	Cu 5.10 Ni 15.92	,,	4.6	1.58	43.0 148.2	5.11 15.89	+0.01 −0.03
3	Cu 5 10 Ni 42.44	,,	,,	1.58	42.8 396.5	5.09 42.50	−0.01 +0.06
4	Cu 20.40 Ni 5 31	,,	18.4	1.62	171.6 49.6	20.40 5.32	Nil +0.01
5	Cu 40.80 Ni 5 31	,,	36.8	1 63	343.6 49.5	40.85 5.31	+0.05 Nil
6	Cu 5.10 Ni 5.31	5	4.6	1.85	42.9 49.4	5.10 5.30	Nil −0.01
7	,,	3	,,	1 98	43.1 49.1	5.13 5.26	+0 03 −0.05
8	,,	2	,,	2.10	43.8 48.7	5.21 5.22	+0.11 −0.09
9	,,	1	,,	2.42	45.0 47.0	5.35 5.04	+0.25 −0.27
10	Cu 5.19 Ni 121.20	10	4.8	1.62	43 6 —	5.18 —	−0.01 —

TABLE IV

No.	Metals taken.	Sulphuric acid (1N).	Reagent solution.	p_H.	Wt. of salts.	Metals found.	Error.
1	Cu 10.20 mg Mn 12.41	20 c.c.	9.2 c.c.	1.05	85.9 mg. 123.0	10 21 mg. 12 42	+0.01 mg. +0.01
2	Cu 5 10 Mn 18.62	,,	4.6	1.02	42.8 184.4	5.09 18.62	−0.01 Nil
3	Cu 4.08 Mn 37 23	,,	3.8	1.06	34.2 369.0	4 07 37.27	−0.01 +0.04
4	Cu 15.30 Mn 4.96	,,	13 7	1.08	128.8 49 0	15.31 4.95	+0 01 −0.01
5	Cu 40.80 Mn 4.96	,,	36 8	1.10	343.4 49.2	40 83 4.97	+0 03 +0.01
6	Cu 5.10 Mn 6.21	10	4.6	1.60	42.9 61.5	5.10 6 21	Nil Nil
7	,,	6	,,	1.74	43.4 61 0	5.16 6.16	+0.06 −0.05
8	,,	5	,,	1.85	44.5 59.5	5.29 6.01	+0.19 −0 20
9	,,	3	,,	2.10	47.0 55.6	5 59 5.62	+0.49 −0 59
10	Cu 5.19 Mn 131.20	20	4.8	1.15	43.8 —	5.20 —	+0.01 —

TABLE V

No.	Metals taken.	Sulphuric acid (1N).	Nitric acid (2N).	Reagent solution.	p_H.	Wt. of copper salt.	Copper found.	Error.
1	Cu 11.59 mg. Ag 9.46	35 c.c.	—	11.6 c.c.	0.96	97.4 mg.	11.58 mg.	−0.01 mg.
2	Cu 34.78 Ag 9.46	,,	—	34.8	1.02	293.1	34.85	+0.07
3	Cu 5.19 Ag 118.30	,,	—	5.2	1.04	43.6	5.18	−0.01
4	Cu 5.80 Ag 236.50	,,	—	5.8	0.98	48.7	5.80	Nil
5	Cu 5.80 Ag 9.46	27	—	,,	1 08	49.0	5 83	+0.03
6	Cu 5.80 Ag 9.46	25	—	,,	1.12	49.5	5.89	+0.09
7	Cu 5.80 Ag 9.46	20	—	,,	1.20	51.5	6.12	+0 32
8	Cu 5.80 Pb 7.20	—	5 c.c.	,,	0.95	48.8	5.80	Nil
9	Cu 11.59 Pb 7.20	—	,,	11.6	0.96	97.7	11.62	+0.03
10	Cu 34 78 Pb 7.20	—	,,	34.8	1.10	293.3	34.87	+0 09
11	Cu 5.80 Pb 54.00	—	,,	5.8	1.02	48.7	5.79	−0.01
12	Cu 5.80 Pb 7.20	—	1	5.8	1.52	48.7	5.79	−0.01
13	Cu 5 80 Pb 7.20	—	0.8	,,	1.65	49.1	5.84	+0.04
14	Cu 5.80 Pb 7 20	—	0.2	,,	2.02	50.2	5.97	+0.17

(*b*) *Separation of Copper from Silver, Mercury and Lead.*—The p_H of the solution was kept 0.96-1.08 for the separation from silver and at 0.95-1.52 for the separation from lead. In the latter case the acidity was controlled with nitric acid (2*N*). Copper was estimated as before. At a higher p_H than what mentioned above, silver and lead were found to co-precipitate. The results are shown in Table V.

In presence of mercury, copper was precipitated from a solution which was treated with an excess of ammonia to keep both copper and mercury in solution. This strongly ammoniacal solution was diluted and heated to boiling after the addition of the reagent. The precipitate was then digested for a few minutes, filtered and washed rapidly with hot water, whereby the mercury salt of the reagent remained completely in solution. Results are shown in Table VI.

TABLE VI

No.	Metals taken	Reagent solution.	Wt. of copper salt	Copper found.	Error.
1	Cu 5.80 mg. Hg 7..6	5.5 c.c.	48.9 mg.	5.81 mg.	+0.01 mg.
2	Cu 11.59 Hg 7 06	10.6	97.4	11.58	−0.01
3	Cu 34.78 Hg 7 06	31.0	293.5	34.90	+0.12
4	Cu 5.80 Hg 17 65	5.5	48.8	5 80	Nil
5	Cu 5 80 Hg 22.94	5.5	49 8	5.92	+0.12
6	Cu 5.80 Hg 28.24	5.5	52.2	6.21	+0.41
7	Cu 34.78 Hg 35.31	31.0	312.0	37.10	+2.32
8	Cu 34.78 Hg 35.31	31 0	308 2	36.64	+1.86

In experiment 8 (Table VI) the quantity of dilute ammonia added was double that used in Expt. 7. During the separation of mercury from copper, the amount of mercury should not exceed 17-18 mg. per 200 c.c. solution containing 10 c.c. of 1 :2 ammonia (30%) (copper=5.80 mg.). High results due to co-precipitation were obtained when the amount of mercury was greater than the mentioned limit.

(*c*) *Separation of Copper from Beryllium.*—The separation was effected by maintaining the p_H of the solution at 1.90-2.35. Beryllium co-precipitated above p_H 2.35.

As the beryllium salt of the reagent was soluble in hot water, the separation could also be done by precipitating copper from boiling hot solution and filtering the same rapidly, washing with hot water, etc. Thus copper (5.19 mg./200 c.c.) was estimated in acid medium in presence of five times its amount of beryllium (25.98 mg./200 c.c.). In presence of larger quantities of beryllium the method failed and there the separation was done in ammoniacal tartrate solution (cf. separation from zirconium given below). The results are shown in Table VII.

TABLE VII

No.	Metals taken.	Sulphuric acid (1N).	Reagent solution.	p_H.	Wt. of copper salt.	Copper found.	Error.
1	Cu 4.64 mg. Be 2.03	5 c.c.	4.2 c.c.	1.90	39.0 mg.	4 64 mg.	Nil
2	Cu 23.18 Be 2.03	,,	21.0	2.05	195.6	23.26	+0 08 mg.
3	Cu 4.64 Be 24.36	,,	4.2	1.94	38.9	4.63	−0.01
4	Cu 5.19 Be 60.90	,,	4.8	1.92	43.6	5 18	−0.01
5	Cu 4.64 Be 2.03	2	4.2	2.35	39.3	4.67	+0.03
6	Cu 4.64 Be 2.03	1	,,	2.50	40.2	4 78	+0.14
7	Cu 4.64 Be 2.03	2	,,	2.32	38.9	4.63	−0 01
8	Cu 4.64 Be 2.03	1	,,	2.45	39.0	4.64	Nil
9	Cu 4.64 Be 2.03	0.4	,,	2.90	38.9	4.63	−0.01
10	Cu 4.64 Be 2.03	0.1	,,	3.62	39.1	4 65	+0.01
11	Cu 4.64 Be 2.03	0.05	,,	4.95	39.0	4.64	Nil
12	Cu 5.19 Be 25.98	0.1	4.8	3.75	43.6	5.18	−0.01
13	Cu 5.19 Be 28.42	0.1	,,	3.72	44.6	5.30	+0.11
14	Cu 5.19 Be 32.50	,,	,,	3.70	47.0	5.59	+0.40
15	Cu 5.19 Be 32.50	—	,,	6.90	43.7	5.20	+0.01
16	Cu 5.19 Be 60.90	—	,,	7.20	43.6	5.18	−0.01

The experiments 1-6 were done by simple control of p_H as referred to in the procedure. Co-precipitation began over p_H 2.35. In experiments 7-12, attempts were made to separate copper from beryllium by precipitating the copper from a boiling solution and digesting the copper precipitate before hot filtration and washing. If the concentration of beryllium was greater than 26 mg. in 200 c.c. solution, beryllium was precipitated with copper even when the solution was digested for a pretty long time (cf. experiments No. 13 and 14). In ammoniacal tartrate solution copper could be easily separated from beryllium (cf. experiments No. 15 and 16).

(*d*) *Separation of Copper from Thorium, Zirconium and Uranium.*—The p_H of the solution was adjusted at 1.80-2.08 and 1.55-1.65 during separation from thorium and uranium respectively. They, however, co-precipitated above p_H 2.08 and 1.65 respectively.

Zirconium could not be separated by simple p_H control as the zirconium salt, like copper salt, is sparingly soluble even at a p_H 0.95. It was, however, separated in presence of a tartrate. The solution containing both copper and zirconium was treated with sodium tartrate (2 g.) and neutralised with dilute ammonia till slightly ammoniacal, or acidified with 1 c.c. of $N/10$ sulphuric acid after neutralisation with ammonia. This was then diluted, heated to boiling and the copper salt precipitated as before. The results are shown in Table VIII.

TABLE VIII

No	Metals taken.	Sodium tartrate.	Sulphuric acid (1*N*),	Reagent solution.	p_H.	Wt. of copper salt.	Copper found	Error. (mg.)
1	Cu 5.80 mg. Th 6.20	—	5 c.c.	5.5 c.c.	1.85	48.7 mg.	5.79 mg.	−0.01
2	Cu 5.80 Th 62 00	—	,,	55	1.80	48.8	5.80	Nil
3	Cu 29.00 Th 6.20	—	,,	26.5	1.86	244.6	29.08	+0.08
4	Cu 5.80 Th 6.20	—	3	5.5	2 08	49.1	5.84	+0.04
5	Cu 5.80 Th 6 20	—	2	,,	2.20	51.0	6.06	+0.26
6	Cu 5.80 Zr 4.83	2 g.	0.1	,,	3.70	48 9	5.81	+0.01
7	Cu 11.60 Zr 4.83	,,	,,	10.6	3.72	97.4	11.58	−0.02
8	Cu 29.00 Zr 4.83	,,	,,	26.5	3.80	244.5	29.08	+0.08
9	Cu 5.80 Zr 28.98	,,	,,	5.5	3.76	48 7	5 79	−0 01
10	Cu 5.19 Zr 57.96	,,	,,	5.2	3.75	43.6	5.18	−0.01
11	Cu 5.80 Zr 4 83	,,	—	5.5	7.50	48.8	5.80	Nil
12	Cu 5.80 Zr 28.98	,,	—	5 5	7.20	48.7	5.79	−0.01
13	Cu 5.19 Zr 57.96	,,	—	5.2	6.70	43.7	5.20	+0.01
14	Cu 5.80 U 5.06	—	10	5.5	1.55	48.8	5.80	Nil
15	Cu 5.80 U 45.54	—	,,	5.5	1.60	48.9	5 81	+0.01
16	Cu 11.59 U 5.06	—	,,	10.6	1.58	97.4	11.58	−0.01
17	Cu 29.00 U 5.06	—	,,	26.5	1.65	244.4	29.06	+0.06
18	Cu 5.80 U 5.06	—	7	5.5	1.74	49.2	5 85	+0.05
19	Cu 5.80 U 5.06	—	5	5.5	1.86	52 6	6.25	+0 45

(*e*) *Separation of Copper from Iron*^{III}, *Aluminium, Chromium*^{III} *and Titanium*^{IV}.— The p_H of the solution was kept at 1.25-1.90, 1.72-2.25, 2.75-2.92 for the separation from iron^{III}, aluminium and chromium^{III} respectively. These elements were found to co-precipitate over p_H 1.90, 2.25 and 2.92 respectively. By this method iron could not be separated when present in more than 12.90 mg./200 c.c. solution (Cu = 5.19-5.80 mg./200 c.c.) as it was precipitated along with copper salt. However, iron even to the extent of 77.7 mg./200 c.c. was separated from copper (5.19 mg./200 c.c.) in ammoniacal tartrate solution according to the method given above (cf. separation from zirconium). By the latter procedure copper was also estimated in presence of titanium^{IV}. The results are shown in Table IX.

TABLE IX

No.	Metals taken.	Sulphuric acid (1N)	Reagent solution.	p_H.	Wt. of copper salt.	Copper found.	Error. (mg.)
1	Cu 5.80 mg. Fe 4.86	5 c.c.	5.5 c.c	1.82	48.8 mg	5.80 mg.	Nil
2	Cu 29.00 Fe 4.86	,,	26.5	1.90	244.4	29.06	+0.06
3	Cu 5.80 Fe 12.90	,,	5.5	1.80	48.7	5.79	−0.01
4	Cu 5.19 Fe 17.10	20	5.2	1.25	44.2	5.26	+0.07
5	Cu 5.19 Fe 27.20	20	5.2	1.32	48.0	5.71	+0.52
6	Cu 5.19 Fe 15.19	5	4.8	1.85	44.8	5.33	+0.14
7	Cu 5.19 Fe 25.90	5	4.8	1.88	49.2	5.85	+0.66
8	Cu 5.80 Fe 4.86	3	5.5	2.05	49.2	5.85	+0.05
9	Cu 5.80 Fe 4.86	2	5.5	2.20	50.8	6.04	+0.24
*10	Cu 5.19 Fe 25.90	—	4.8	6.82	43.7	5.20	+0.01
*11	Cu 5.19 Fe 77.70	—	4.8	6.75	43.6	5.18	−0.01
12	Cu 5.19 Al 4.72	5	4.8	1.75	43.5	5.18	−0.01
13	Cu 25.95 Al 4.72	5	23.6	1.85	218.8	26.02	+0.07
14	Cu 5.19 Al 48.40	5	4.8	1.82	43.7	5.20	+0.01
15	Cu 5.19 Al 4.72	2	4.8	2.25	43.9	5.22	+0.03
16	Cu 5.19 Al 4.72	1	4.8	2.40	44.4	5.28	+0.09
17	Cu 5.19 Cr 4.85	0.6	4.8	2.78	43.7	5.20	+0.01
18	Cu 25.95 Cr 4.85	0.6	23.5	2.80	218.6	25.99	+0.04
19	Cu 5.19 Cr 50.10	0.6	4.8	2.75	43.6	5.18	−0.01
20	Cu 5.19 Cr 4.85	0.4	4.8	2.92	43.8	5.21	+0.02
21	Cu 5.19 Cr 4.85	0.3	4.8	3.30	44.2	5.26	+0.07
*22	Cu 5.19 Ti 57.50	—	4.8	6.95	43.6	5.18	−0.01
*23	Cu 5.19 Ti 115.10	—	4.8	6.78	43.7	5.19	Nil
*24	Cu 5.19 Ti 115.10	—	4.8	—	43.6	5.18	−0.01

*The separations were done in ammoniacal tartrate solutions.

(*f*) *Separation from Vanadium, Molybdenum and Tungsten.*—The p_H of the solution was adjusted at 1.58-1.70 for the separation from vanadium, at 1.55-1.80 and 1.50-1.78 for the separation from molybdenum and tungsten respectively. High results were obtained due to co-precipitation as the p_H was raised above 1.70, 1.80 and 1.78 respectively. Results are shown in Table X. Separation could also be done in an ammoniacal solution.

TABLE X

No.	Metals taken.	Sulphuric acid (1N)	Reagent solution.	p_H.	Wt. of copper salt	Copper found.	Error. (mg)
1	Cu 5 19 mg. V 3 54	10 c.c.	4 8 c c	1 62	43.6 mg.	5.18 mg.	−0.01
2	Cu 5.19 V 53.10	10	4.8	1.60	43.6	5.18	−0.01
3	Cu 10.38 V 1 77	10	9 6	1.58	87.4	10.39	+0 01
4	Cu 5.19 V 3.54	7	4.8	1.70	43.9	5.22	+0.03
5	Cu 5.19 V 3 54	6	4.8	1 78	44.4	5.28	+0.09
6	Cu 5.19 Mo 6.72	10	4.8	1.55	43.6	5.18	−0.01
7	Cu 5.19 Mo 67.20	10	4 8	1 60	43 5	5.17	−0.02
8	Cu 20.76 Mo 4.57	10	19.2	1.52	174.8	20.78	+0.02
9	Cu 5.19 Mo 6.72	6	4 8	1.80	43.7	5.20	+0.01
10	Cu 5 19 Mo 6.72	5	4.8	1 90	44.0	5 23	+0.04
11	Cu 5.19 W 5 74	10	4 8	1.50	43.5	5 17	−0.02
12	Cu 5 19 W 91 84	10	4.8	1.55	43 6	5.18	−0.01
13	Cu 25.95 W 5.74	10	23.5	1.54	219.0	26.04	+0.09
14	Cu 5.19 W 5.74	6	4.8	1.78	43.8	5.21	+0.02
15	Cu 5.19 W 5.74	5	4.8	1 85	44.6	5.30	+0.11

(*g*) *Separation from Bismuth, Antimony and Tin*^{IV}.—For the estimation of copper in presence of bismuth, the p_H of the solution was maintained below 1.65 over which the co-precipitation began. Copper was separated from antimony^{III} and tin^{IV} in ammoniacal tartrate solution as described before (cf. Procedure *d*). The results are shown in Table XI.

TABLE XI

No.	Metals taken.	Sodium tartrate.	Sulphuric acid (1N).	Reagent solution.	p_H.	Wt. of copper salt.	Copper found.	Error. (mg.)
1	Cu 5 19 mg. Bi 5 78	—	12 c c.	4.8 c.c.	1.40	43 6 mg.	5.18 mg.	−0.01
2	Cu 5.19 Bi 156.00	—	12	4.8	1.44	43.5	5 17	−0.02
3	Cu 25.95 Bi 5.78	—	12	23.5	1.50	219.2	26 06	+0.11
4	Cu 5.19 Bi 5 78	—	8	4.8	1.65	43.9	5.22	+0.03
5	Cu 5.19 Bi 5 78	—	7	4.8	1.72	44.8	5.34	+0.15
6	Cu 5.19 Sb 95 45	2 g.	—	4.8	6.40	43.7	5.20	+0.01
7	Cu 5.15 Sb 190.90	4	—	4.8	6.58	43.6	5.18	−0 01
8	Cu 5.19 Sn 135 20	2	—	4.8	7.65	43.8	5.21	+0.02
9	Cu 5.19 Sn 210.40	4	—	4 8	7.80	43.7	5.20	+0.01

Experiments 6-9 were done in ammoniacal tartrate solution.

(*h*) *Separation from Mixtures of Thorium, Uranium, Aluminium, Chromium, Vanadium, Molybdenum, Tungsten and Bismuth.*—Copper was estimated in ammoniacal tartrate solution (cf. procedure *d*) in presence of three different mixtures of the elements mentioned above. The results are shown in Table XII.

TABLE XII

Cu = 5.19 mg.

No.	Metals taken		Sodium tartrate.	Reagent solution.	p_H.	Copper salt.	Copper found.	Error.
1	Al	9.44 mg						
	Cr	9.70						
	Bi	11.56						
	U	10.12	3 g.	5.2 c c.	7.90	43.6 mg.	5.18 mg.	−0.01 mg.
	Th	6.20						
	Mo	6.72						
	W	5.74						
	V	7.08						
	Al	18.88						
	Cr	19.40						
	Bi	23.12						
	U	20.24	4	6.0	8.15	43.8	5.21	+0.02
	Th	12.40						
	Mo	13.54						
	W	11.48						
	V	14.16						
3	Al	37.76						
	Cr	38.80						
	Bi	34.66						
	U	25.36	6	8.0	8.98	43.5	5.17	−0.02
	Th	18.60						
	Mo	19 80						
	W	16.72						
	V	21 24						

(*i*) *Separation from Rare-earths.*—This separation was done also from ammoniacal tartrate solution. Results are shown in Table XIII.

TABLE XIII

No.	Metals taken.		Sodium tatrrate.	Reagent solution.	p_H.	Copper salt.	Copper found.	Error. (mg.)
1	Cu	5.19 mg.	2 g.	8 o mg.	8.58	43.8 mg	5.21 mg.	+0.02
	ΣR_2O_3	140.90						
2	Cu	5.19	4	8.0	9.20	43.8	5.21	+0.02
	ΣR_2O_3	281.80						
3	Cu	5.19	4	8.0	9.26	43.9	5.22	+0.03
	ΣR_2O_3	281.80						

In conclusion it can be said that the reagent benzoquinaldinic acid may be used for the estimation of copper and its separation from almost all the elements, a large number of which is separated by a simple p_H control and a few by complexing with some masking agents.

Further work on the use of the reagent for the estimation of other elements and their separations are in progress and are shortly to be communicated.

One of us (A. K. D.) welcomes this opportunity to thank Messrs. Calcutta Chemical Co. Ltd., for the award of a research fellowship.

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FORMATION OF COMPLEX COMPOUNDS BETWEEN ALKALI CHLORIDES AND ALKALINE EARTH CHLORIDES. PART I. SYSTEM KCl—$BaCl_2$—H_2O

By L. N. Srivastava and P. C. Bose

Viscosity of a series of mixed solutions of potassium chloride and barium chloride was determined by Ostwald's method and viscosity plotted against the only variant, viz. concentration of barium chloride. The graph shows seven definite kinks which correspond to the following compounds: 4KCl. $BaCl_2$, 3 KCl. $BaCl_2$, 2 KCl. $BaCl_2$, 2KCl.3$BaCl_2$, 3KCl. 2$BaCl_2$, KCl $BaCl_2$ and KCl.2$BaCl_2$.

Barium chloride is known to form double salts with potassium chloride in the fused state as well as in the aqueous solution. A brief summary of the work done on the subject, as given below, shows four such compounds, viz. 2 KCl.$BaCl_2$, 3 KCl.$BaCl_2$, KCl. 3 $BaCl_2$ and KCl.2$BaCl_2$ which have been reported as existing either in the fused state or in the aqueous solution.

Vortisch (*Jahrb. Min. Beil. Bo.*, 1914, **38**, 186) has shown that with barium chloride, potassium chloride forms the compound 2KCl.$BaCl_2$, m.p. 680°. The compounds 2KCl.$SrCl_2$ and 2 KCl.$BaCl_2$ are isomorphous and rhombic.

Gemsky (*J. Chem. Soc.*, 1914, **106**, 51) obtained the data for the binary system $BaCl_2$-KCl and the m.p. of $BaCl_2$.2 KCl recorded was 663°.

Elchardus and Laffitte (*Bull. soc. chim.*, 1932, **51**, 1572) showed by thermal analysis of the system KCl-$BaCl_2$ the existence of a eutectic at a concentration of 42.75 mol.% of barium chloride corresponding to the compound 3KCl.$BaCl_2$ and transition point at 347°, corresponding to the compound KCl.3$BaCl_2$. There is no evidence for the KCl.2$BaCl_2$.

Sato (*Kinz. No. Kenk*, 1933, **10**, 448) recorded the equilibrium data for binary mixtures of barium chloride and potassium chloride. This system yields a compound of the formula 2 KCl.$BaCl_2$, m.p. 1760°.

Spacu and Popper (*Z. physikal. Chem.*, 1899, **B30**, 113) established the existence in solutlon of a complex anion corresponding to the compound of the formula $(BaCl_4)K_2$ and $BaCl_5(H_2O)BaK$ by refractometric investigation.

It was thought desirable to undertake a thorough investigation of mixed aqueous solutions of potassium chloride and barium chloride to find out the actual number and nature of possible complexes.

We have examined a variety of physico-chemical properties, e.g., viscosity, density, refractive index, freezing point and conductivity the of system KCl-$BaCl_2$-H_2O yielding results leading to identical conclusions.

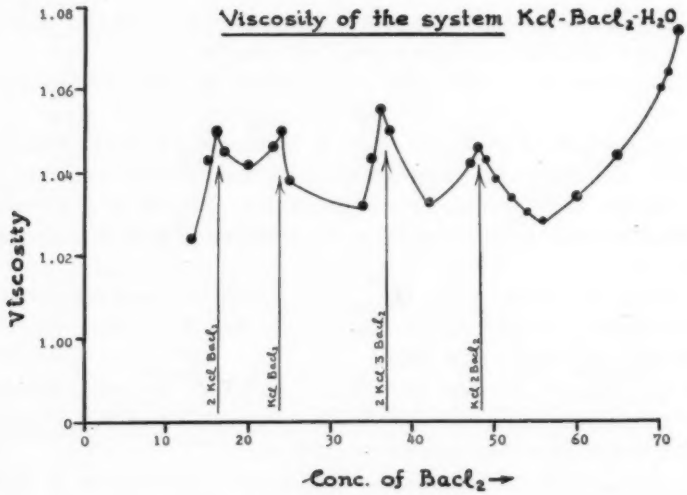
Experimental

The method of monovariation was adopted which consisted in preparing a large number of solutions, with only one varying factor, namely, the concentration of one of the reactants. The advantage of this method can well be understood by comparing the results of Narashimhamurti (*Proc. Ind. Acad. Sci.*, 1950, **31A**, 160) on the one hand

and that of Nayar and Pande (*ibid.*, 1948, **27A**, 298, 284) on the other, both of them working on the same problem. The former's method of procedure was continued variation in which he obtained a very irregular graph, while that obtained by Nayar and Pande was regular and self-explanatory.

The substances used were of A.R. quality (B.D.H). A stock solution (0.5*M*) was prepared by dissolving the calculated weight of the salt and making up in a standard flask using conductivity water. A 250 c.c. standard flask was taken and 24 c.c. of potassium chloride solution were run into it from a standard burette. The requisite volume of barium chloride was then added from another standard burette and the mixture was made up to the mark with conductivity water. In this manner 32 solutions were prepared in all of which the concentration of potassium chloride was kept constant, namely, 0.125*M* and that of barium chloride was systematically varied from 0.0*N* to 0.25*M*. These solutions were stored in steamed reagent bottles. All operations were carried out in a thermostat maintained at 30° ±0.05°. The compositions of these solutions are shown in the figures.

FIG. 1



The densities of these solutions were determined by the pyknometer method, and viscosity by means of an Ostwald viscometer.

The values of viscosity were then plotted against the concentration of the variant, viz. barium chloride. The plots indicate seven definite kinks at places corresponding to 6, 8, 12, 16, 24, 36, 48 c.c. of barium chloride solution (vide Figs. 1 and 2). Since 24 c.c. of potassium chloride solution are present in each case, the above points represent the formation of compounds in which the stoichiometric ratios between potassium chloride and barium chloride are 4:1, 3:1, 2:1, 2:3, 1:1 3:2 and 1:2 respectively. Thus seven complexes viz. $4KCl.BaCl_2$, $3KCl.BaCl_2$, $2KCl.BaCl_2$, $2KCl.3BaCl_2$, $KCl.BaCl_2$, $3KCl.2BaCl_2$ and $KCl.2BaCl_2$ are shown to exist in the solution. Four of

FIG. 3

FIG. 2

FIG. 3

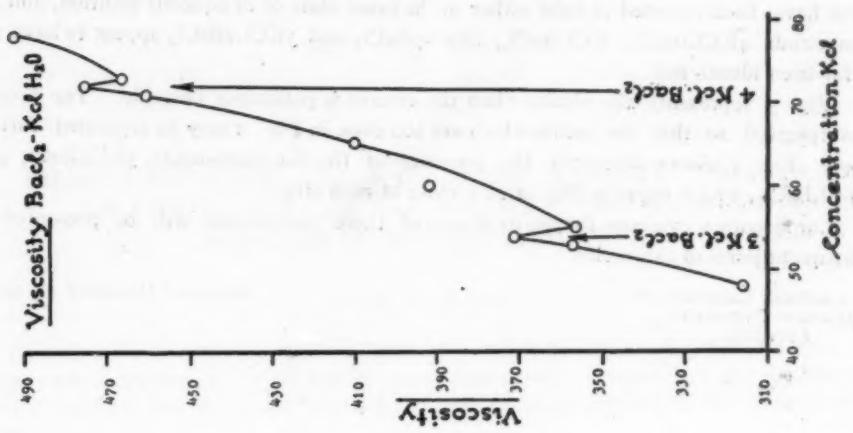
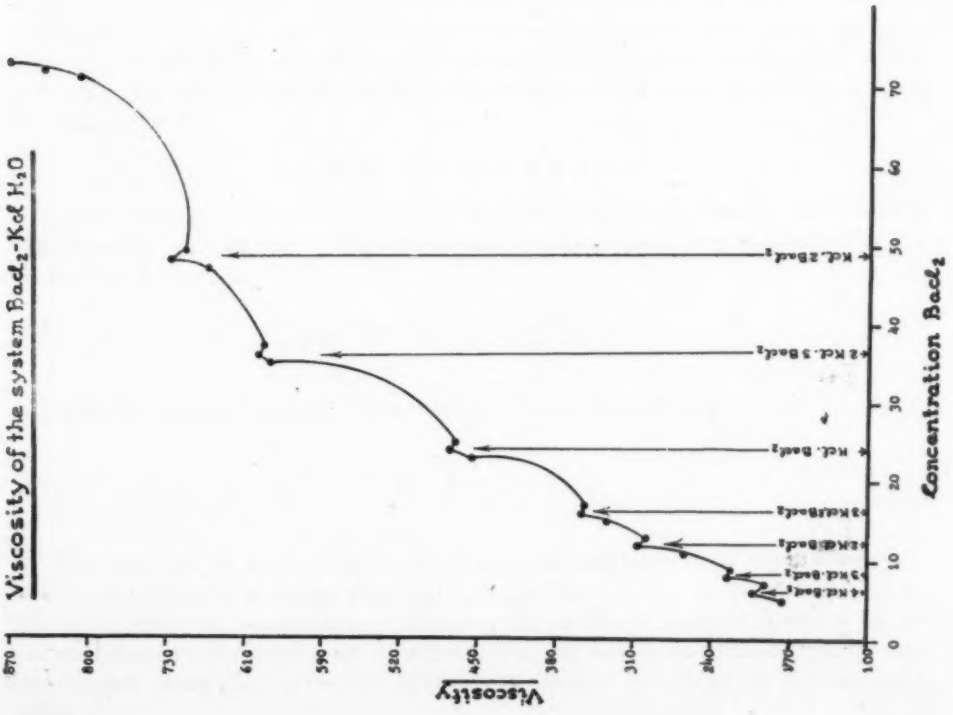

Viscosity $BaCl_2$-Kcl H_2O
4 Kcl. $BaCl_2$
3 Kcl. $BaCl_2$
Viscosity
Concentration Kcl

FIG. 2


Viscosity of the system $BaCl_2$-Kcl H_2O
Kcl. $2BaCl_2$
2 Kcl. $3BaCl_2$
Kcl. $BaCl_2$
Viscosity
Concentration $BaCl_2$

these have been reported to exist either in the fused state or in aqueous solution, and the compounds $4KCl.BaCl_2$, $KCl.BaCl_2$, $2KCl.3BaCl_2$ and $3KCl.2BaCl_2$ appear to have not so far been identi- fied.

Fig. 3 represents the results when the variant is potassium chloride. The process was reversed so that the points which are too close in Fig. 2 may be separated further apart. Fig. 3 shows distinctly the presence of the two compounds, $3KCl.BaCl_2$ and $4\ KCl.BaCl_2$, which occur in Fig. 2 very close to each other.

Confirmatory evidence for the existence of these compounds will be presented in subsequent parts of this series.

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CHARGE AND STABILITY OF COLLOIDS. PART XVI. KINETICS OF COAGULATION OF As_2S_3 SOL WITH AND WITHOUT ADDITION OF NON-ELECTROLYTES

By H. R. Lodha

The influence of the non-electrolytes like amyl alcohol, ethylmethyl ketone, diethyl ketone, acetoacetic ester, paraldehyde, etc. on the kinetics of coagultion of As_2S_3 sol according to the Smoluchowski equation has been studied. It has been observed that the non-electrolytes mentioned slow down the process.

In a previous communication (Chatterji and Lodha, this *Journal*, 1951, **28**, 131) the effect of non-electrolytes on the adsorption of oppositely charged ions has been studied. It has been observed that the addition of non-electrolytes like *n*-amyl alcohol, *iso*amyl alcohol, methyl acetate, ethyl acetate, ethylmethyl ketone, diethyl ketone, acetoacetic ester, etc. protects the As_2S_3 sol and the adsorption of oppositely charged ions is increased. In the present investigation the author has endeavoured to study the kinetics of coagulation of As_2S_3 sol in presence of the same non-electrolytes with a view to ascertaining if there is any difference in the velocity of coagulation of the As_2S_3 sol offered by such protection. A method similar to that of Paine (*Koll.-Chem. Beih.*, 1912, **4**, 24) has been followed.

Experimental

The procedure followed here is the same as adopted by Yadava and Chatterji (this *Journal*, 1944, **21**, 227). The coagulation velocity constant was determined by the Smoluchowski equation

$$\gamma_1 = \frac{\gamma_0}{(1+\beta t)^2} \quad \text{or} \quad \beta = \frac{1}{t}\left(\sqrt{\frac{a}{a-x}} - 1\right).$$

The bimolecular constant, k, was determined from the equation

$$k = \frac{1}{t} \cdot \frac{x}{a-x}.$$

The number of particles of the original sol has been taken to be proportional to γ and the concentration of the sol after time t, denoted by $a-x$, to be proportional to γ_1. The doubt about the concentration representing the number of particles vanishes as the process followed is the same in all the experiments, and hence, the method gives the relative changes taking place in the sol. The results obtained are shown in the following tables.

TABLE I

Conc. of the As_2S_3 sol = 17.98 g./litre. 5 c c. sol + 0.55 c.c. of $N/20$-$BaCl_2$ + the requisite amount of water to make the total vol. = 10 c.c.

Time.	$a-x$.	$\beta \times 10^3$.	$k \times 10^3$.
0.0 min.	0.08990 g.	0.0	0.0
10	0.08091	5.3	11.11
20	0.07911	3.3	6.82
30	0.07642	2.4	5.88
40	0.07462	2.42	5.11
50	0.07192	2.40	5.00
60	0.07012	2.16	4.70

In the following tables the columns 'a-x' have been omitted in order to condense the tables.

TABLE II

Volume of 2% amyl alcohol.

	0.5 c.c.		1.0 c c.		1.5 c c.		2.0 c.c.	
Time.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.
0.0 min.	0.0	0.0	0.0	0.0	0 0	0.0	0.0	0 0
10	5 38	12.66	20.3	46 51	8.55	8.54	5.82	12.66
20	4.08	8.60	10.15	23.25	2.91	6.33	2.91	6.33
30	1.94	4.16	6.76	15.50	1.94	4 16	1.94	4.16
40	1.36	3.16	5 07	11.60	1.45	3.16	1 45	3 16
50	1.16	2.53	1 71	2.70	1 16	2.53	1.16	2.53
60	0.97	2.11	0.97	2.11	0 97	2.11	0 97	2.11

TABLE III

5 c.c. sol + 0.55 c.c. $BaCl_2$ ($N/20$) + increasing amount of 8% ethylmethyl ketone + requisite amount of water. Total vol. = 10 c.c.

Volume of 8% ethyl methyl ketone.

	0 5 c.c.		1.0 c.c.		1 5 c.c.		2.0 c c	
Time.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$
0.0 min.	0.0	0.0	0 0	0 0	0.0	0 0	0.0	0.0
10	5.30	16 74	5.82	12.65	2.03	46.51	2.03	46 51
20	2 03	23 25	2.91	6 33	1 96	4.27	3.42	11 34
30	1.02	15.50	2.28	4.93	1.94	4 22	2.13	5.74
40	0.98	21.36	1.71	3.65	1.45	1.16	2 63	5.67
50	1.16	17.09	1.64	3 44	1.75	2.81	2.10	4.53
60	1.40	3.10	1.36	2.87	1.55	2.78	2.10	4.50

TABLE IV

5 c.c. sol + 0.55 c.c. $BaCl_2$ + increasing amount of 4% diethyl ketone + requisite amount of water. Total vol. = 10 c.c.

Volume of 4% diethyl ketone.

	0.5 c.c.		1.0 c.c.		1.5 c.c.		2.0 c.c	
Time.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.
0 0 min	0.0	0.0	0.0	0.0	0.0	0 0	0 0	0.0
10	8 26	17.22	20.30	46.91	5 90	14.27	20 3	46 51
20	4.11	8.61	4.11	8 61	4.11	4.273	4.11	12.17
30	2.74	6.15	3.74	11.01	3.73	5.74	3.94	11 06
40	2.05	4.31	2.95	8 26	3 75	5 53	2.62	5.53
50	1.64	3.46	2.36	6 61	2.54	5 48	1.64	6.61
60	1.42	3.07	1.75	3 68	2 12	4 57	1.75	3.68

TABLE V

Volume of 8% paraldehyde.

	0 5 c.c.		1 0 c.c.		1.5 c.c.		2.0 c.c.	
Time	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.
0 0 min.	0.0	0.0	0.0	0 0	0.0	0 0	0.0	0 0
10	4 93	10.64	3.44	7.85	9.14	19.82	10.91	23.28
20	3.61	8.31	1.72	3.92	4.57	9 93	6.12	13.44
30	3 04	6.62	2.11	4.26	3.04	6 62	4.08	9 58
40	2.73	5.82	1.81	4.18	3.06	6.72	3.51	7 71
50	2 44	5.63	1 82	3 96	2.44	5.37	2 81	6.17
60	2 34	5.14	1.80	5.14	2.64	5.61	2 34	5.14

TABLE VI

Volume of 4% acetoacetic ester.

	0 5 c.c.		1.0 c.c.		1 5 c.c.		2.0 c.c	
Time.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.	$\beta \times 10^3$.	$k \times 10^3$.
0 0 min.	0 0	0 0	0.0	0.0	0.0	0 0	0.0	0.0
10	12 24	26.88	15.84	15.84	33.66	33.66	14 04	30.84
20	7 02	15 42	8.95	19.58	7.92	16.83	7.92	16 84
30	5.26	10.28	5.97	13.05	5.28	11.22	5.96	13.05
40	3 51	7 71	4 48	9.79	3.96	8.41	4.48	9.879
50	2.81	6 17	3.58	7.83	3.56	7 83	3.58	7.83
60	2.64	5.61	3.27	7.31	2.98	6.525	3.27	7 31

From the above tables it follows that β remains fairly constant when no non-electrolyte is added. With the addition of non-electrolytes β initially increases and then goes

on decreasing gradually. This gradual decrease may be intimately connected with protection, because if the stability of the colloid is increased, the velocity of coagulation should slow down, which is to be expected from the fact that increase of these non-electrolytes produces stability (*loc. cit.*). The initial tendency of increase in β value is a characteristic of a rapid coagulation which is in confirmity with the observation of previous workers. Thus, we see that the character of coagulation of the same sol changes gradually on addition of non-electrolytes.

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CHARGE AND STABILITY OF COLLOIDS. PART XVII. EFFECT OF NON-ELECTROLYTES

BY H. R LODHA

Effect of non-electrolytes like *n*-amyl alcohol, ethyl and methyl acetates, diethyl ketone and *n*-hexyl alcohol on the stability of positively charged ferric hydroxide sol has been studied and thecharge on the colloidal particles calculated from the amount of chemical adsorption.

In continuation of our previous communication (this *Journal*, 1953, **30**, 415) in the present paper the work has been extended with the same purpose in view, to the positively charged ferric hydroxide sol. Under limitations as pointed out in earlier communications, the charge on the colloid particles has been calculated from the amount of chemical adsorption alone.

EXPERIMENTAL

The experimental procedure followed here is the same as given in Part XVI (*loc. cit.*). The results obtained are shown in the following table.

TABLE I

Sol taken = 5 c.c. Total vol. = 10 c.c. Time of coagulation = 1 hr.

Conc. of sol = 2.132 g./litre.		Conc. of sol = 4.264 g./litre.	
n-Amyl alcohol (2%).	Coagulation conc. of $N/40$-K_2SO_4.	Methyl acetate (6%).	Coagulation conc. of $N/40$-K_2SO_4.
0.0 c.c.	0.2 c.c.	0.0 c.c.	0.30 c.c.
0.5	0.25	0.5	0.25
1.0	0.30	2.5	0.225
2.0	0.20	4.0	0.30

In the following tables the adsorption of oppositely charged ions by the particles of ferric hydroxide sol, when non-electrolytes (same as used in Part XVI, *loc. cit.*) are added in varying concentrations, are given.

TABLE II

Variation in the adsorption of SO_4'' by the particles of ferric hydroxide sol when 2% n-amyl alcohol is added in increasing concentrations.

Conc. of the sol = 2.132 g./litre. Radius of particles = 50 $\mu\mu$. Sol taken = 200 c c. Total vol. = 400 c.c. No. of particles in the sol taken = 1.1×10^{14}.

Nature of the sol.	$N/40$-K_2SO_4 added.	Adsorption of SO_4''			Charge × 10 e. s. u.
		Total.	Physical.	Chemical.	
Sol + water	4.0 c.c.	0.0022 g.	0.0005 g.	0.0017 g.	8.3
,, + ,, + 10 c.c. alcohol	5.0	0.0071	0.0057	0.0014	7.0
,, + ,, + 20 ,,	6.0	0.0086	0.0069	0.0017	8.3
,, + ,, + 30 ,,	4.0	0.0022	0.0006	0.0016	7.5

TABLE III

Variation of the adsorption of SO_4'' by the particles of the ferric hydroxide sol when 6% ethyl acetate is added in increasing amounts.

Conc. of the sol = 2.132 g./litre. Radius of the particles = 50 $\mu\mu$. Sol taken = 100 c.c. Total vol. = 200 c.c. No. of particles in the sol taken = 1.1×10^{14}.

Nature of the sol.	$N/40$-K_2SO_4 added.	Adsorption of SO_4''			Charge × 10^5 e. s. u.
		Total.	Physical.	Chemical.	
Sol + water	5.0 c c.	0.0022 g.	0.0005 g.	0.0017 g.	8.3
,, + ,, + 10 c.c. Et Ac	4.0	0.0044	0.0026	0.0018	8.7
,, + ,, + 20 ,,	5.0	0.0036	0.0022	0.0014	7.0
+ ,, + 50 ,,	6.0	0.0032	0.0020	0.0012	5 8
, + ,, + 60 ,,	5.0	0.0032	0.0020	0.0012	5.8
,, + ,, + 80 ,,	4.0	0.0016	0.0006	0.0010	5.0

TABLE IV

Variation of the adsorption of SO_4'' by the particles of ferric hydroxide sol when 6% methyl acetate is added in increasing amounts.

Conc. of the sol. = 4.264 g./litre. No. of the particles in the sol taken = 2.15^{14}. Other conditions same as in Table III.

Nature of the sol.	$N/40$-KSO_4 added.	Adsorption of SO_4''			Charge × 10^5 e. s. u.
		Total.	Physical.	Chemical.	
Sol + water	4.0 c.c.	0.0078 g.	0.0046 g.	0.0032 g.	8.5
,, + ,, + 10 c.c. Me Ac	5.0	0.0070	0.0036	0.0034	9.0
,, + ,, + 50 ,,	5.0	0.0068	0.0032	0.0036	9 5
,, + ,, + 80 ,,	6.0	0.0074	0.0042	0.0032	8.5

TABLE V

Variation of the adsorption of SO_4'' by the particles of the ferric hydroxide sol when 0.5% hexyl alcohol is added in increasing amounts.

Conditions same as in Table IV.

Nature of the sol.	$N/40$-K_2SO_4 added.	Adsorption of SO_4'' Total.	Physical.	Chemical.	Charge × 10^5 e. s. u.
Sol + water	6.0 c.c.	0.0078 g.	0.0046 g.	0.0032 g.	8.5
,, + ,, + 10 c.c Hx OH	5.0	0.0082	0.0052	0.0032	8.5
,, + ,, + 20 ,,	6.0	0.0096	0.0062	0.0034	9.0
,, + ,, + 30 ,,	5.0	0.0072	0.0042	0.0030	7.99

TABLE VI

Variation of the adsorption of SO_4'' by the particles of ferric hydroxide sol when 4% diethyl ketone is added in increasing amounts.

Conditions same as in Table IV.

Nature of the sol.	$N/40$-K_2SO_4 added.	Adsorption of SO_4'' Total.	Physical.	Chemical.	Charge × 10^5 e. s. u.
Sol + water	6.0 c.c.	0.0078 g.	0.0046 g.	0.0032 g.	8.5
,, + ,, + 30 c.c. Et_2CO	4.0	0.0062	0.0034	0.0028	7.6
,, + ,, + 40 ,,	4.5	0.0069	0.0042	0.0027	7.5
,, + ,, + 90 ,,	6.0	0.0099	0.0069	0.0030	8.0

From the results it appears that on addition of the non-electrolytes to the ferric hydroxide sol, the sol is stabilised to varying degrees. It is also inferred that on increasing the concentration of the non-electrolytes there is no appreciable increase in the charge. The stabilisation may be explained on the basis of film formation around the particles (Freundlich), the cutting down of the adsorption of the precipitating ion by the adsorption of the non-electrolytes (Weiser, *J. Phys. Chem.*, 1924, **28**, 1253), to a decrease in the interfacial tension (Chowdhury, *ibid.*, 1928, **32**, 1481) or by the increase in the complex forming tendency between the colloid and the protective non-electrolyte (Pauli and Kitaz).

The results of the above tables when compared with those of the previous communication (*loc. cit.*) undoubtedly show the independence of the effect of the non-electrolyte as to the nature of the charge (whether positive or negative). At the same time it has been observed that protective action has not of necessity depended upon a strong charge having been communicated to the sol. It appears therefore that when protection takes place, the charge on the colloidal particle should not necessarily increase.

The author's most sincere thanks are due to Dr. A. C. Chatterji under whose guidance the work was carried out and to the U. P. Govt. for the award of a research fellowship.

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THE UNIVERSITY, LUCKNOW.

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INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART IV. THE SYSTEM KCl—$HgCl_2$—H_2O

By Miss Hemlata J. Kazi and C. M. Desai

With dilution of the mixed salt solution of potassium and mercuric chlorides in water, the number of molecular compounds between these salts has been found to increase from three to six to seven.

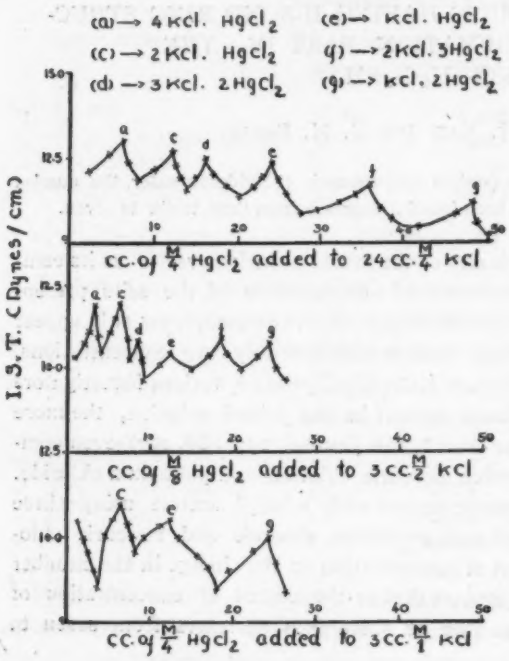
It has been observed that the complexity of the mixed solutions varies as its composition is changed with respect to the extent of concentration of the salts present in it (unpublished). In the system $LiNO_3$—$Pb(NO_3)_2$—H_2O, two complexes only appear within certain range of salt concentrations, while at comparatively low concentrations, three complexes become evident. In the system KCl—$HgCl_2$—H_2O, various investigators have reported different number of complexes present in the mixed solution, the more important being three. In an earlir paper (Part I, this *Journal*, 1953, **30**, 287) seven complexes have been shown to be formed between mercuric chloride and potassium chloride. In the present paper interfacial tension measurements with *n*-butyl acetate using three more comparatively high concentrations of each potassium chloride and mercuric chloride have been made to ascertain the effect of concentration on the change in the number of complexes present in this system. It appears that as the extent of concentration of both the salts in solution increases, the number of complexes decreases from seven to six to three.

Experimental

In the case of one pair of stock solutions ($M/4$) of potassium chloride and mercuric chloride each, prepared in distilled water, 24 c.c. of potassium chloride were poured from a burette into a 100 c.c. measuring flask to which the requisite volume of mercuric chloride was added and the total volume made up to 100 c.c. by addition of water. In the second case, a stock solution of potassium chloride ($M/2$) and that of mercuric chloride ($M/8$) were prepared and 3 c.c. of potassium chloride were pipetted into a flask to which the requisite volume of mercuric chloride was added and then the total volume made up to 30 c.c. with water. In the third case, a stock solution of potassium chloride ($M/1$) and that of mercuric chloride ($M/4$) were prepared and 3 c.c. of potassium chloride were pipetted into a flask to which the requisite volume of mercuric chloride was added and then the total volume made up to 30 c.c. with water. In this way, a series of mixed solutions was prepared by the method of monovariation from each of the three pairs of stock solutions of potassium chloride and mercuric chloride for interfacial tension measurements. The composition of the mixed solutions and the corresponding interfacial tension values are reproduced in Fig. 1.

Seven complexes appear in mixed solutions, prepared from stock solutions $M/80$, $M/40$ (Part I, *loc. cit.*) and six complexes in those prepared from $M/4$ each of potassium and mercuric chlorides. They are of the molecular formulae: (*a*) 4 KCl. $HgCl_2$, (*b*) 3KCl. $HgCl_2$, (*c*) 2KCl. $HgCl_2$ (*d*) 3KCl. 2 $HgCl_2$, (*e*) KCl.$HgCl_2$, (*f*) 2KCl. 3$HgCl_2$ and (*g*) KCl. 2 $HgCl_2$; the complex (*b*) 3KCl.$HgCl_2$ disappears in the case of the series prepared from $M/4$ stock solutions. The same six complexes also appear in comparatively high concentrations of mixed solutions prepared from $M/2$-KCl and $M/8$-$HgCl_2$ solutions. With still higher concentrations of mixed solutions, prepared from $M/1$-KCl and $M/4$-$HgCl_2$, only three complexes (*c*), (*e*) and (*g*) appear. Thus, the extent of concentration of salts in mixed solutions determines largely the number of complexes formed; at lower concentrations, the formation of greater number of complexes appears to be favoured.

FIG. 1


(a)→ 4 KCl. HgCl2
(c)→ 2 KCl. HgCl2
(d)→ 3 KCl. 2 HgCl2
(e)→ KCl. HgCl2
(f)→ 2 KCl. 3 HgCl2
(g)→ KCl. 2 HgCl2
I. S. T. (Dynes/cm.)
cc. of M/4 HgCl2 added to 24 cc. M/4 KCl
cc. of M/8 HgCl2 added to 3 cc. M/2 KCl
cc. of M/4 HgCl2 added to 3 cc. M/1 KCl

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INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART V. THE SYSTEM NH_4Cl—$HgCl_2$—H_2O

By Miss Hemlata J. Kazi and C. M. Desai

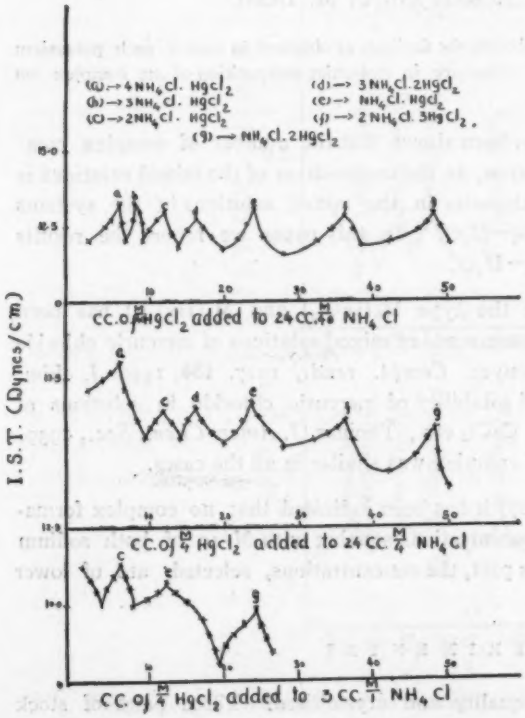
The number of complexes, formed between ammonium and mercuric chlorides in their mixed solutions, has been found to vary from seven to six to three with increase in salt concentrations.

In this paper the results obtained with the system $NH_4Cl-HgCl_2-H_2O$ has been reported. The measurements with *n*-butyl acetate were carried out, starting with a number of concentrations of NH_4Cl and $HgCl_2$ stock solutions, as it has been observed that the complexity of the mixed solutions changes with change in its composition.

Experimental

The salts used were of standard quality and recrystallised. Two stock solutions, $M/4$ and $M/40$ of ammonium chloride and mercuric chloride each, were prepared in distilled water; 24 c.c. of ammonium chloride were poured from a burette into a 100 c.c. measuring flask to which a requisite volume of mercuric chloride was added and the total volume made up to 100 c.c. with water. In the third case, stock solutions of ammonium chloride ($M/1$) and mercuric chloride ($M/4$) were prepared in distilled water; ammonium chloride solution (3 c.c.) was pipetted into a flask to which a requisite volume of mercuric chloride was added and the total volume made up to 30 c.c. In this way a series of mixed solutions was prepared by the method of monovariation from each of the three pairs of stock solutions of ammonium and mercuric chlorides for interfacial tension measurements. The composition of the mixed solutions and the corresponding interfacial tension values are shown in Fig. 1.

Fig. 1


(a) → 4 NH4Cl. HgCl2
(b) → 3 NH4Cl. HgCl2
(c) → 2 NH4Cl. HgCl2
(d) → 3 NH4Cl. 2 HgCl2
(e) → NH4Cl. HgCl2
(f) → 2 NH4Cl. 3 HgCl2
(g) → NH4Cl. 2 HgCl2
I.S.T. (Dynes/cm)
cc. of M/4 HgCl2 added to 24 cc. M/4 NH4Cl
cc. of M/4 HgCl2 added to 24 cc. M/4 NH4Cl
cc. of M/4 HgCl2 added to 3 cc. M/1 NH4Cl

The results, obtained with this system, are parallel to those obtained with KCl – $HgCl_2$ – H_2O system, with respect to the number of complexes, their molecular composition and range of concentration (cf. Part IV this *issue*, p 421). Three, six and seven complexes appear to be favoured with decreasing extent of salt concentrations in mixed solutions. They are (1) a, b, c, d, e, f and g; (2) a, c, d, e, f, g and (3) c, e, and g. indicated in Fig. 1.

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INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART VI. THE SYSTEM $NaCl-HgCl_2-H_2O$

BY MISS HEMLATA J. KAZI AND C. M. DESAI

The results obtained with this system collaborate the findings as obtained in case of such potassium and ammonium chloride systems, with the difference in molecular composition of one complex out of six when complexes are evident.

In previous parts of this series it has been shown that the number of complex compounds varies from three to six to seven, as the composition of the mixed solutions is changed to decreasing concentration of the salts in the mixed solutions in the systems $KCl-HgCl_2-H_2O$ and $NH_4Cl-HgCl_2-H_2O$. In this paper we report the results obtained with the system $NaCl-HgCl_2-H_2O$.

The presence of the compounds of the type $M(HgCl_3)$ and $M_2(HgCl_4)$ has been indicated by means of ebullioscopic measurements in mixed solutions of mercuric chloride and alkali chlorides (Bourion and Ronyer, *Compt. rend.*, 1927, **184**, 1449; *J. chim. phys.*, 1928, **25**, 234). From the data of solubility of mercuric chloride in solutions of various chlorides, such as HCl, LiCl, $CaCl_2$ etc., Thomas (*J. Amer. Chem. Soc.*, 1939, **61**, 920) suggested that the $(HgCl_2.Cl)^-$ complex was similar in all the cases.

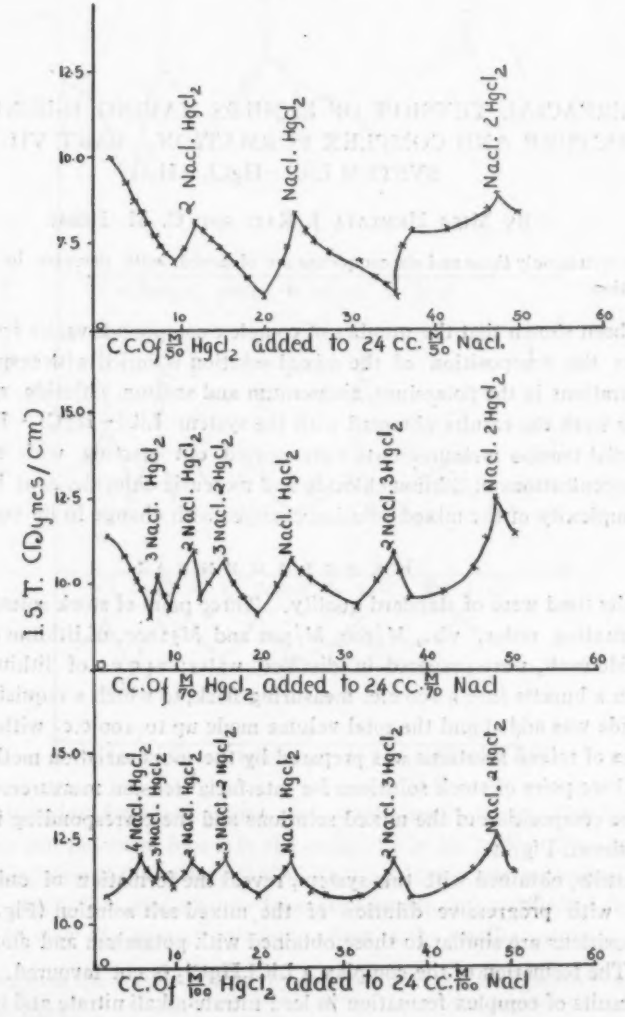
In Part I (this *Journal*, 1953, **30**, 287) it has been indicated that no complex formation seems to have been formed at concentrations starting with $M/40$ of both sodium chloride and mercuric chloride. In this part, the concentrations, selected, are of lower order.

EXPERIMENTAL

The salts used were of standard quality and crystallised. Three pairs of stock solutions $M/50$, $M/70$, $M/100$ of sodium chloride and mercuric chloride each were pre-

pared in distilled water; 24 c.c. of sodium chloride were poured from a burette into a 100 c.c. measuring flask to which a requisite volume of mercuric chloride was added and the total volume made up to 100 c.c. with water. In this way a series of mixed solutions was prepared by the method of monovariation from each of the three pairs of the above stock solutions for interfacial tension measurements with *n*-butyl acetate. The composition of the mixed solutions and the corresponding interfacial tension values are reproduced Fig. 1.

FIG. 1.



Formation of three, six and seven complexes appears to be favoured with decreasing extent of salt concentrations in mixed solutions as in the case of other two systems.

However, it is interesting to observe that formation of the complex $3NaCl.HgCl_2$ is preferentially favoured with the disappearence of the complex $4\ NaCl.HgCl_2$, when six complexes altogether are formed (Fig. 1)., while with KCl and NH_4Cl systems, the opposite is the case.

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INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART VII. THE SYSTEM $LiCl-HgCl_2-H_2O$

BY MISS HEMLATA J. KAZI AND C. M. DESAI

With this system,only three and six complexes are observed, with decrease in salt concentrations in mixed solution.

It has been shown that the number of complex compounds varies from three to six to seven as the composition of the mixed solution is varied with respect to decreasing salt concentrations in the potassium, ammonium and sodium chloride systems. In this part of the work the results obtained with the system $LiCl-HgCl_2-H_2O$ are reported. The interfacial tension measurements were carried out starting with a number of decreasing concentrations of lithium chloride and mercuric chloride, as it has been evident that the complexity of the mixed solution changes with change in its composition.

EXPERIMENTAL

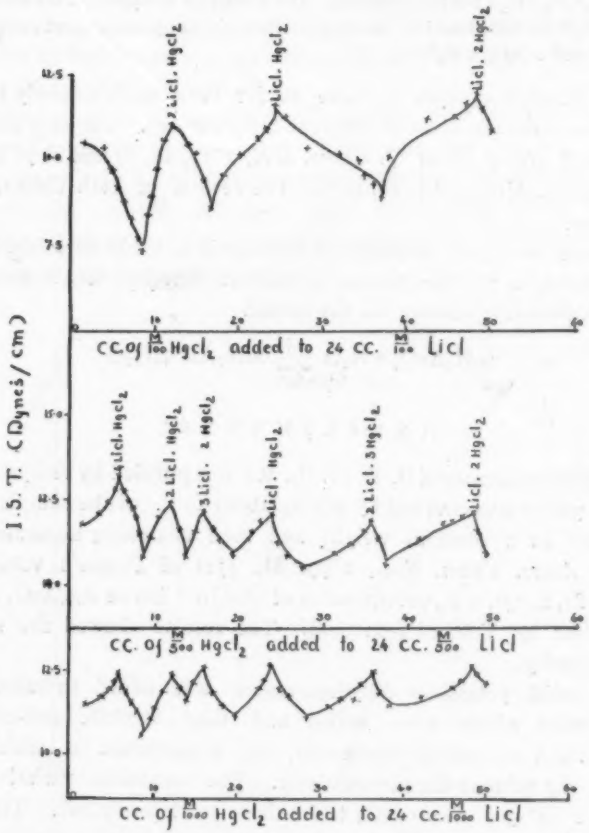
The salts used were of standard quality. Three pairs of stock solutions, in decreasing concentration order, viz., $M/100$, $M/500$ and $M/1000$, of lithium chloride and mercuric chloride each, were prepared in distilled water; 24 c.c. of lithium chloride were poured from a burette into a 100 c.c. measuring flask, to which a requisite volume of mercuric chloride was added and the total volume made up to 100 c.c. with water. In this way a series of mixed solutions was prepared by the mor.ovariation method from each of the above three pairs of stock solutions for interfacial[1] tension measurements with *n*-butyl acetate. The composition of the mixed solutions and the corresponding interfacial tension values are shown Fig. 1.

The results, obtained with this system, reveal the formation of only three and six complexes with progressive dilution of the mixed salt solution (Fig. 1). Their molecular compositions are similar to those obtained with potassium and ammonium chloride systems. The formation of the complex $3\ LiCl.HgCl_2$ is not favoured.

The results of complex formation in lead nitrate-alkali nitrate and mercuric chloride-alkali chloride systems reveal interesting observation. To obtain maximum possible

number of complexes, dilution of alkali salt solution should be progressively increased in the order: Li > Na > K. Under this condition, the ions get comparatively far apart and interionic attractions between anions and alkali metal ions tend to become negligible. The dilution of a solution involves work against electrostatic attraction, and hence, the extent of dilution required for this purpose is a measure of the magnitude

FIG. 1.


I.S.T. (Dynes/cm)
cc. of M/100 HgCl2 added to 24 cc. M/100 LiCl
cc. of M/500 HgCl2 added to 24 cc. M/500 LiCl
cc. of M/1000 HgCl2 added to 24 cc. M/1000 LiCl

of electrostatic attraction between anions and alkali metal ions. This binding force between the anions and the metal ions is in the order: Li > Na > K. This is in agreement with decreasing size of the cations ($Li^+ < Na^+ < K^+$) and correspondingly increasing deformation effect (*i.e.* the change from electrovalence to covalence) in the order: $Li^+ > Na^+ > K^+$, in view of a greater polarising effect of the smaller cation.

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SYSTEM POTASSIUM (DIHYDROGEN) ARSENATE—WATER

By Ram Chand Paul, Kundan Lal, V. S. Gaind and S. S. Bawa

The system $KH_2AsO_4-H_2O$ has been studied. The transition temperature for the change $KH_2AsO_4.H_2O \rightarrow KH_2AsO_4+H_2O$ has been found to be 59.6°. Eutectic temperature and composition have been determined as -3.61° and 20.15% KH_2AsO_4.

No regular attempt appears to have so far been made to study the solubility of potassium dihydroarsenate in water at different temperatures. The only available data as to its solubility at 6° are by Field (*J. Chem. Soc.*, 1859, **11**, 6) and at 7° by Muthamann and Kuntze (*Z. Kryst. Min.*, 1894, **23**, 368). The results of both these attempts appear to be contradictory.

In the present work, an attempt has been made to study its solubility in water at different temperatures, e. g., the system potassium dihydroarsenate-water as a whole including the transition temperature for the system

$$KH_2AsO_4 + H_2O \rightleftarrows KH_2AsO_4.H_2O$$

Experimental

Potassium dihydroarsenate of B. D. H. (L. R.) was purified by recrystallising it twice from water. Its purity was checked by drying about 10 g. of the sample in an electric oven at 100°-110° to a constant weight and then analysing according to Bennets' modification (*J. Amer. Chem. Soc.*, 1899, **21**, 431) of Pearce's volumetric method (*Chem. News*, 1883, **1**, 14), e.g., precipitation of $(AsO_4)'''$ ion as Ag_3AsO_4 and subsequent estimation of silver by Volhard's method. The results showed the sampleto be of 99.85 to 99.95% purity.

Excess of solid potassium dihydroarsenate was added to about 10 c.c. of water in glass tubes which were sealed and then tumbled end-over-end in an electrically heated and controlled thermostat, the temperature of which was regulated with the help of a toluene thermo-regulator. The maximum variation of temperature in the range 15°-50° was 0.05°, while above 50° it was 0.10°. The attainment of equilibrium condition was studied by breaking different tubes after two hourly intervals and analysing the solutions for their $(AsO_4)'''$ content, by the method already given. The equilibrium condition was reached in solutions up to 50° in 8 hours and above 50° in 6 hours, but in no case less than 12 hours' shaking was given. Before breaking a tube for analysis of the solution, it was held stationary in the bath for about ½ hour during which interval all the solid in suspension settled down. Seal was then broken and the clear supernatant liquid taken out with the help of a pipette, previously heated in the same bath, by keeping it in a wide bore glass tube, sealed at the lower end. The solid was also taken in some cases, pressed dry between folds of filter paper and analysed for approximate water content.

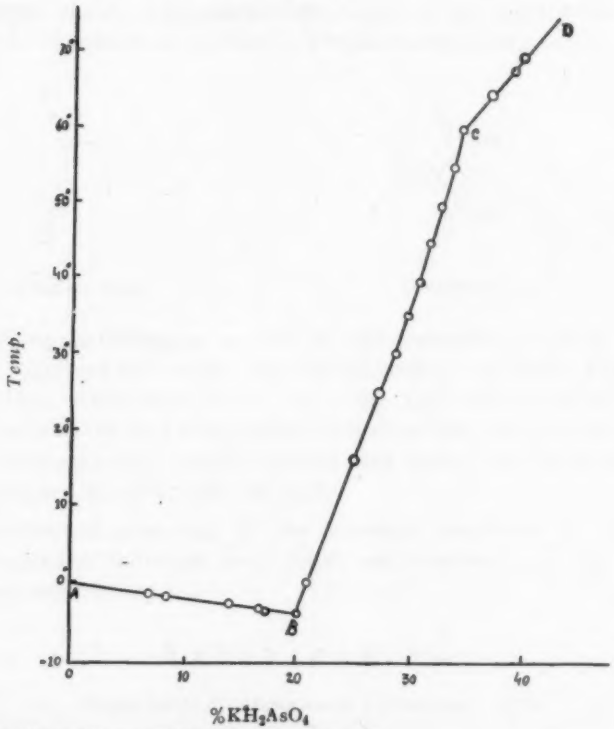
For solubility at 0° the method given above was not applied due to difficulty in maintaining the bath at this temperature. Here solutions of strength slightly less than that required for a saturated condition at 18° were prepared and cooled to 0° in ice-water mixture kept in a large thermos flask. The solution, where separation of solid just appeared on stirring with a glass rod at 0°, was allowed to remain in the thermos for an hour. The supernatant liquid was then analysed for its arsenate content.

Between the concentration of solutions at 0° and pure water, six solutions of exactly known strength were prepared and the depression in freezing point of water in these solutions found out by Beckmann's cryoscopic method. Saturated solution of ice and common salt was used as the cooling bath.

During the determination of depression of freezing point for ice line, the solutions were allowed to cool gradually to temperatures lower than the freezing point of water. In most of the cases it was found that the temperature became constant at about -3.60°. In solutions containing 20.15% KH_2AsO_4 only one freezing point, e. g., -3.61° was observed. The results show that the cryohydric temperature is -3.61°.

The results are shown graphically in Fig. 1.

FIG. 1



The results show the transition temperature of

$$KH_2AsO_4 . H_2O \rightleftarrows KH_2AsO_4 + H_2O$$

is 59.6°.

Line AB represents the ice line. Line BC shows the solubility of solid $KH_2AsO_4.H_2O$ with increase of temperature and the line CD, solubility of anhydrous KH_2AsO_4. The solid phases present along BC and CD are $KH_2AsO_4.H_2O$ and KH_2AsO_4. B is the cryohydric point with composition of 20.15% KH_2AsO_4 and temperature $-3.61°$. Point C represents the transition point of the system $KH_2AsO_4.H_2O \rightarrow KH_2AsO_4 + H_2O$. This has also been confirmed by the thermometric method by plotting the heating and cooling curves of $KH_2AsO_4.H_2O$ and $KH_2AsO_4 + H_2O$ mixture.

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MALONATO AND OXALATO COMPLEXES OF TRIVALENT METALS. PART I. MALONATO COMPLEXES OF ALUMINIUM AND GALLIUM

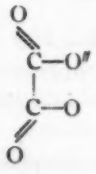
By Nihar Kumar Dutt and Miss Promita Bose

Several *tris*-malonato complexes of aluminium and gallium have been prepared and described. Sodium, potassium and ammonium salts have been shown to have compositions analogous to those of the corresponding oxalato complexes.

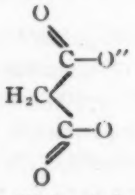
Various complex oxalates of trivalent metals like aluminium, chromium, iron and cobalt have been prepared and successfully resolved.

Wahl (*Ber.*, 1927, **60**, 399) prepared and resolved the aluminium compound $[Al(C_2O_4)_3]'''$. Sodium, potassium and ammonium complex oxalates of gallium have been prepared and described by Neogi and Dutt (this *Journal*, 1938, **15**, 83). The latter salts have also been resolved by the same authors.

Malonic acid ($C_3H_4O_4$) is the higher homologue of oxalic acid ($C_2H_2O_4$) with a three-carbon atom chain. Like oxalato ion, C_2O_4'', it may also function as a bidentate group taking two co-ordination positions in a regular octahedron,



[Oxalato ion].



[Malonato ion].

While studying the absorption spectra of chromi-oxalates, Lapraik (*Chem. News*, 1893, **67**, 219) prepared and studied the corresponding complexes of Cr with malonic acid. Jaegar (*Akad. Amsterdam Versl.*, 1917, **26**, 190), claimed to have resolved the chromi-malonates with the help of strychnine, but stated that the resolved salts racemised very quickly. Malonato complexes of trivalent iron have been prepared and studied by Scholz and Jaeger (*Monatsh*, 1908, **29**, 442).

The preparation and properties of the malonato complexes of aluminium and gallium, which resemble tervalent iron, cobalt and chromium, form the subject matter of the present communication.

Experimental

Alkali Salts of Aluminium Trimalonato Acid

Potassium Trimalonato-aluminate.—A solution of acid potassium malonate was prepared from malonic acid and the requisite quantity of KOH solution. A freshly

precipitated aluminium hydroxide was digested with the malonate solution on a water-bath till it practically went into solution leaving a small undissolved residue. The mixture was then filtered, concentrated on the water-bath and allowed to crystallise in a vacuum desiccator over concentrated sulphuric acid. The crystals separating were filtered under suction and dried in air.

The substance forms beautiful colorless crystals, readily soluble in water but insoluble in alcohol. The substance is stable in the solid state as well as in solution. Ammonium hydroxide precipitates alumiuium hydroxide only on keeping and boiling. [Found : Al, 5.24, 5.56 ; K, 23.30, 23.18, 23.41. $K_3Al(C_3H_2O_4)_3.3H_2O$ requires Al, 5.36 ; K, 23.21 per cent].

Sodium trimalonato-aluminate was similarly prepared by digesting aluminium hydroxide with acid sodium malonate. The sodium salt resembles the potassium salt very closely but is somewhat more soluble. [Found : Al, 5.63, 6.05; Na, 14.88 ; 15.31. $Na_3Al(C_3H_2O_4)_3.3H_2O$ requires Al, 5.92 ; Na, 15.13 per cent].

Ammonium trimalonato-aluminate was prepared by digesting aluminium hydroxide with ammonium hydrogen malonate as in the previous cases. The salt crystallised with one molecule of water like the corresponding iron compound.

It resembles the other salts in all respects. It is the most soluble in the series. [Found : Al, 6.52, 6.72 ; N, 10.21 ; 10.18. $(NH_4)_3Al(C_3H_2O_4)_3.H_2O$ requires Al, 6.66, N, 10.37 per cent].

Alkali Salts of Gallium Trimalonato Acid

Potassium trimalonato-galliate was prepared by a method very similar to that for the corresponding salt of aluminium by digesting gallium hydroxide with potassium hydrogen malonate and crystallising the resulting solution. Like the aluminium salt, it crystallises with three molecules of water.

In properties, it resembles the corresponding aluminium compound in all respects. [Found : Ga, 12.49, 12.65 ; K, 21.62 ; 21.22. $K_3Ga(C_3H_2O_4)_3.3H_2O$ requires Ga, 12.63 ; K, 21.43 per cent].

Sodium trimalonato-galliate was prepared in the same way as above by using sodium hydrogen malonate and gallium hydroxide. [Found : Ga, 14.05, 13.87 ; Na, 13.72, 13.69. $Na_3Ga(C_3H_2O_4)_3.3H_2O$ requires Ga,13.95; Na, 13.85 per cent].

Method of Analysis.—The aluminium and gallium were estimated after decomposition of the complex salts with strong sulphuric acid and precipitated as hydroxide. Sodium and potassium were estimated in the filtrates as sulphates. Nitrogen was estimated by Kjeldahl's method.

Determinationas of the stabilities of above and other malonato complexes of trivalent metals are in progress.

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SEARCH FOR NEW INSECTICIDES. PART VI

By A. B. Sen and A. K. Sen Gupta

Several ethers of *ortho*-chlorophenols have been prepared with a view to testing them for their insecticidal activity.

In continuation of the work in Part V (this *Journal*, 1953, **30**, 59) we have now prepared a large number of ethers of chlorinated *o*-allylphenols. These ethers containing a neurotoxic halobenzene group and an ether linkage having lipophilic properties may be expected to be good contact insecticides (Tien-Chin Chen and Summerford, *J. Amer. Chem. Soc.*, 1951, **73**, 4694). The *o*-allylphenols were prepared from, *o*-chloro-, *p*-chloro- and 2:4-dichloro-phenols by the Claisen rearrangement of the respective allyl ethers of these phenols (Claisen, *Annalen*, 1913, **401**, 36) and were then converted into methyl, ethyl, propyl, allyl, benzyl and *o*-chlorobenzyl ethers. The methyl ethers were prepared in the usual way by alkylation with dimethyl sulphate; alkyl halides were employed in the case of ethyl and propyl ethers; the allyl, benzyl and *o*-chlorobenzyl ethers were obtained by refluxing a mixture of the appropriate chlorinated allylphenols with an equivalent amount of allyl bromide, benzyl or *o*-chlorobenzyl chloride respectively and freshly fused potassium carbonate in acetone, on a water-bath for 8 hours (Tien-Chin Chen *et al.*, *loc. cit.*).

Experimental

Allyl Ethers of Chlorophenols.—The allyl ethers of *p*-chloro-, *o*-chloro- and 2:4-dichloro-phenols were prepared by refluxing a mixture of the appropriate phenol (1*M*) with an equivalent amount (1*M*) of allyl bromide and freshly fused potassium carbonate (1*M*) in acetone on a water-bath for 6 hours in the usual way (Claisen, *Annalen*, 1919, **418**, 97). The boiling points and the yields obtained are approximately the same as reported earlier (Claisen, *loc. cit.*).

Table I

Name of the compound.	Found		Reported earlier	
	B.P.	Yield.	B.P.	Yield.
Allyl ether of 2-chlorophenol	108°-110°/12 mm.	90%	109°/12 mm.	90%
Allyl ether of 4-chlorophenol	107°-108°/12	95	106°-107°/12	90
Allyl ether of 2:4-dichlorophenol	144°-145°/25	92	144°-145°/25	85

Allylchlorophenols.—The above allyl ethers of chlorophenols were refluxed for 6 hours on the wiregauze in order to rearrange them to allylchlorophenols and then isolated in the usual way (Claisen, *loc. cit.*). The boiling points and yields are recorded below.

Table II

Name of the compound.	Found		Reported earlier	
	B.P.	Yield.	B.P	Yield.
2-Allyl-4-chlorophenol	124°-125°/12 mm.	94%	122°-124°/12 mm.	94%
2-Allyl-6-chlorophenol	127°-129°/12	85	125°-126°/12	90
2-Allyl-4:6-dichlorophenol	122°-125°/6	86	120°/6	90

Ethers of Allylchlorophenols.—Methyl ethers were prepared from dimethyl sulphate (1 *M*), chloroallylphenols (1 *M*) and 10% sodium hydroxide in the usual way (Ullmann, *Annalen*, 1905, **340**, 208).

Ethyl and propyl ethers were prepared from the corresponding alkyl halides (1 *M*), chloroallylphenols (1 *M*) and sodium ethoxide in the usual way (Cahours, *ibid.*, 1851, **78**, 226).

o-Chlorobenzyl, benzyl and allyl ethers were obtained by refluxing a mixture of allylchlorophenol (0.1 *M*), an equivalent amount of *o*-chlorobenzyl chloride, benzyl chloride or allyl bromide (1 *M*), freshly fused potassium carbonate (0.1 *M*.) and 100 c.c. of acetone on a water-bath for 8 hours. After cooling, water was added and the mixture was extracted with ether, the ethereal layer was separated and dried over freshly fused potassium carbonate. The ether was then removed and the residual liquid was distilled under reduced pressure (cf. Tien-Chin Chen *et al.*, *loc. cit.*).

TABLE III

Ethers.	B.P.	Yield.	Mol. formula	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found	% Hydrogen. Calc
Methyl ether of							
2-Allyl 4-chlorophenol	104°/30 mm.	75%	$C_{10}H_{11}OCl$	64.06	65.81	5.72	6.0
2- ,, -6 ,,	113°/12	75	$C_{10}H_{11}OCl$	65.0	65.8	5.9	6.0
2- ,, -4 :6-dichlorophenol	143°/30	75	$C_{10}H_{10}OCl_2$	54.9	55.3	4.4	4.6
Ethyl ether of							
2- ,, 4-chlorophenol	152°/20	55	$C_{11}H_{13}OCl$	65.3	66.9	5.95	6.6
2- ,, 6- ,,	163°/17	75	$C_{11}H_{13}OCl$	66.8	66.9	6.0	6.6
2- ,, 4 :6-dichlorophenol	123°/6	75	$C_{11}H_{12}OCl_2$	56.9	57.1	5.18	5.9
Propyl ether of							
2- ,, 4-chlorophenol	125°/6	87	$C_{12}H_{15}OCl$	67.8	68.4	6.81	7.1
2- ,, 6- ,,	129°/5	75	$C_{12}H_{15}OCl$	67.9	68.4	7.0	7.1
2- ,, 4 :6-dichlorophenol	143°/5	62.5	$C_{12}H_{14}OCl_2$	58.7	58.8	5.7	5.73

TABLE IV

Ethers.	B P.	Yield.	Mol. formula.	% Carbon Found.	% Carbon Calc.	% Hydrogen Found.	% Hydrogen Calc.
Allyl ether of							
2-Allyl 4-chlorophenol	138°/11 mm	87%	$C_{13}H_{13}OCl$	68.5	69.06	6.08	6.3
2- ,, 6- ,,	155°/6	80	$C_{12}H_{13}OCl$	68.96	69.06	6.1	6.3
2- ,, 4 :6-dichlorophenol	158°/7	75	$C_{12}H_{11}OCl_2$	58.9	59.3	4.9	4.96
Benzyl ether of							
2- ,, 4-chlorophenol	120°/10	60	$C_{16}H_{15}OCl$	73.65	74.27	5.44	5.8
2- ,, 6- ,,	156°/15	75	$C_{16}H_{15}OCl$	74.08	74.27	5.40	5.8
2- ,, 4 :6-dichlorophenol	145°/6	70	$C_{16}H_{14}OCl_2$	65.44	65.53	4.72	4.78
o-Chlorobenzyl ether of							
2 ,, 4-chlorophenol	126°/10	60	$C_{16}H_{14}OCl_2$	65.5	65.5	4.74	4.79
2 ,, 6- ,,	155°/15	75	$C_{16}H_{14}OCl_2$	65.3	65.5	4.75	4.79
2 ,, 4 :6-dichlorophenol	163°/7	83	$C_{16}H_{13}OCl_3$	57.9	58.6	3.74	3.97

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PREPARATION OF ANTIBACTERIALS FROM ORGANO-MERCURIALS. PART XI. MERCURATED AZO DYES DERIVED FROM DIAZOTISED ACETOXYMERCURI-β-NAPHTHYLAMINE AND 2:4-DIACETOXY-MERCURI-α-NAPHTHYLAMINE

By S. S. Guha Sircar and Mahendra Kumar Rout

Preparation and antibacterial action of a group of mercurated azo dyes derived from diazotised β-naphthylamine and 2:4-diacetoxymercuri-α-naphthylamine have been studied.

The activity of a group of mercurated azo dyes prepared by coupling diazotised acetoxymercuri-β-naphthylamine and 2:4-diacetoxymercuri-α-naphthylamine with a number of mercurated amines and phenols has been studied in the present communication.

Experimental

The methods used by Dimroth and Jacobs and Heidelberger (vide Part VIII, this *Journal*, 1953, **30**, 361) have been employed for the preparation.

Acetoxymercuri-β-naphthylamine or 2:4-diacetoxymercuri-α-naphthylamine was diazotised in acetic acid medium and then coupled with the reagents recorded in parenthesis in column 1 in Tables Ia and b. Column 1 also gives the names of the resulting azo dyes. If the coupling reagent was an amine, coupling was done in acetic acid medium, and if a phenol, coupling was done in alkaline medium.

All the experimental data including the results of biological tests are summarised in Tables Ia and b.

Table Ia

R = $HgOCOCH_3$ = Acetoxymercuri.

Name of the azo dye.	% Hg.		M.p.	Yield.	Colour.	M.E.D.	
	Found.	Calc.				E. Coli.	Staphylo.
(R-β-Naphthylamine-β-azo'-α-naphthylamine (α-naphthylamine)	36.0	36.4	153°	66%	Chocolate	1:200,000	1:20,000
(R-β-Naphthyl-α-azo)-β-naphthylamine (β-naphthylamine)	36.1	36.4	145°	55	Red	1:200,000	1:20,000
(R-β-Naphthylazo)-p-toluidine (p-toluidine)	39.1	40.5	130°	70	Brick-red	1:50,000	1:20,000
(R-β-Naphthylazo)-p-chloroaniline (p-chloroaniline)	36.6	37.0	146°	67	Chocolate-red	1:75,000	1:15,000
(R-β-Naphthylazo)-p-sulphanilic acid (sulphanilic acid)	33.2	34.1	Above 250°	70	Orange-red	1:18,000	1:15,000
-β-Naphthylazo)-anthranilic acid (o-aminobenzoic acid)	36.0	36.3	,, 162°	78	Orange-red	1:20,000	1:30,000
(R-β-Naphthylazo)-m-aminobenzoic acid (m-amin benzoic acid)	36.6	36.3	Above 250°	76	Purple-red	1:16,400	2:15,000
(R-β-Naphthylazo)-p-aminobenzoic acid (p-aminobenzoic acid)	35.8	36.3	170°	75	Red	1:10,000	1:8,000

TABLE IA (contd.)

Name of the azo dye.	% Hg.			M.p.	Yield.	Colour.	M.E.D.	
	Found.	Calc.					E. Coli.	Staphylo.
(R-β-Naphthylazo)-α-naphthol (α-naphthol)	35.6	36.0		142°	75%	Brick-red	1:15,000	1:18,000
(R-β-Naphthylazo)-β-naphthol (β-naphthol)	35.4	36.0		154°	77	Crimson-red	1:15,000	1:18,000
(R-β-Naphthylazo)-thiosalicylic acid (thiosalicylic acid)	35.0	35.4		168°	76	Dull red	1:20,000	1:20,000
(R-β-Naphthylazo)-salicylic acid (salicylic acid)	36.7	36.3		194°	66	Red	1:25,000	1:15,000
(R-β-Naphthylazo)-o-nitrophenol (o-nitrophenol)	35.7	36.3		149°	55	Red	1:6,000	1:10,000
(R-β-Naphthylazo)-resorcinol (resorcinol)	38.6	38.3	Above	270°	62	Reddish brown	1:4,000	1:18,000
(R-β-Naphthylazo)-p-oxybenzoic acid (p-oxybenzoic acid)	36.0	36.3		250°	75	Red	1:20,000	1:15,000
2′-Amino-5-R-(R-β-naphthylazo)-benzene (R-aniline)	53.0	52.4	Abobe	250°	73	Brick-red	1:200,000	1:18,000
2′-Amino-3′-R-5′-chloro-(R-β-naphthylazo)-benzene (R-p-chloroaniline)	50.5	50.1	,,	,,	66	Crimson-red	1:300,000	1:20,000
2′-Dimethylamino-5′-(chloromercuri)-(R-β-naphthylazo)-benzene (chloromercuri-dimethylaniline)	51.4	52.1	,,	,,	74	Dark red	1:400,100	1:25,000
4′-Chloromercuri-(1-Rβ-naphthyl-β-azo)-α-naphthylamine (chloromercuri-α-naphthylamine)	51.0	50.6	,,	,,	65	Dark red	1:400,000	1:25,000

TABLE IB

R = $HgOCOCH_3$ ≡ Acetoxymercuri.

Name of the azo dye.	%Hg.			M.p.	Yield.	Colour.	M.E.D.	
	Found.	Calc.					E. Coli	Staphylo.
(2:4-Di-R-α-naphthyl-β-azo)-α-naphthol (α-naphthol)	48.5	49.5	Above	250°	78%		1:20,000	1:10,000
(2:4-Di-R-α-naphthol-α-azo)-β-naphthol (β-naphthol)	49.0	49.1	,,		84	Pale chocolate	1:18,000	1:12,000
(2:4-Di-R-α-naphthylazo)-salicylic acid (salicylic acid)	50.0	49.5	,,		71	Chocolate	1:15,000	1:8,000
(2:4-Di R-α-naphthylazo)-resorcinol (resorcinol)	51.0	51.3	,,		75	Brownish choc.	1:10,000	1:8,000
(2:4-Di-R-α-naphthylazo)-anthranilic acid (anthranilic acid)	49.0	49.5		200°	80	Purple-red	1:20,000	1:25,000
(2:4-Di-R-α-naphthylazo-m-aminobenzoic acid (m-aminobenzoic acid)	49.2	49.5	Above	250°	82	Purple-chocolate	1:15,000	1:10,000
(2:4-Di-R-α-naphthylazo)-p-aminobenzoic acid (p-aminobenzoic acid)	51.1	49.5		185°	78	,,	1:12,000	1:8,000
2′-Amino-5′-chloro-(2:4-di-R-α-naphthylazo)-benzene (p-chloroaniline)	49.5	50.0	Above	250°	66	Dark red	1:80,000	1:15,000
2′-Chloro-4′-amino (2:4-di-R-α-naphthylazo)-benzene (o-chloroaniline)	50.1	50.0	,,	,,	74	Chocolate-red	1:80,000	1:15,000
2′-Amino-3′-R-5′-chloro-(2:4 di-R-α-naphthylazo)-benzene (R-p-chloroaniline)	57.5	56.9	Above	250°	71	,,	1:400,000	1:25,000
2′-Amino-5′-R-(2:4-di-R-α-naphthylazo)-benzene (R-aniline)	59.2	58.8	,,	,,	70	Dark red	1:300,000	1:25,000

The series of compounds prepared from diazotised acetoxymercuri-β-naphthylamine is characterised by the presence of a naphthalene nucleus in the diazotised part. The dyes of this series show slightly reduced bactericidal values (cf. Parts IX and X, this *Journal*, 1953, **30**, 364, 366). The order of activities is as follows :

Chloromercuri-naphthylamine, chloromercuri-dimethylaniline > mercurated *p*-chloroaniline and aniline; α- and β-naphthylamines ; *p*-chloroaniline > *p*-toluidine > salicylic acid > anthranilic acid, *p*-hydroxybenzoic acid, thiosalicylic acid, sulphanilic acid > *m*-aminobenzoic acid, α- and β-naphthols; *p*-aminobenzoic acid > *o*-nitrophenol, resorcinol.

The series prepared from diazotised 2:4-diacetoxymercuri-α-naphthylamine is distinguished from the above one in the position of the functional NH_2 group and in increased Hg contents. As can be seen, the members of this series are more active than the above one. The activities show a graded order of values which roughly conform to the sequence set forth earlier: mercurated *p*-chloroaniline > mercurated aniline > *p*-chloroaniline ; *o*-chloroaniline > α- and β- naphthol, aminobenzoic acids > resorcinol.

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REVIEWS

Lehrbuch der organischen Chemie.—By Holleman-Richter. 27th & 28th Revised Edition. Published by Messrs Walter De Gruyter & Co., Berlin, 1951, pp. 526.

This book will suit the needs of advanced (Honours and Post-Graduate) students of Chemistry admirably. The advancement of organic chemistry has been so rapid in recent years that it is no easy task to select the more important items suitable for students and to deal with different aspects of the subject without permitting the volume to become unwieldy. The authors have performed this task in a praiseworthy manner. The book first made its appearance about 50 years ago and the fact that no less than 28 editions have come out in the meantime is an eloquent testimony to its popularity and the success of the attempt for the inclusion of the more important and up-to-date informations.

The book is a balanced presentation of fundamental principles of Organic Chemistry together with newer ideas which are indispensable for advanced students. The fundamentals of aliphatic, alicyclic, aromatic and heterocyclic compounds are presented from the points of view of functional groups, structure and synthesis. Physico-chemical aspects such as stereoisomerism, optical activity, strain theory of closed systems and isomerism of benzenoid compounds are discussed without omitting the newer concepts of mesomerism, chain reactions and the like. Biochemical aspects have rightly received special attention, while compounds, old or new, having significance for medicinal or industrial purpose, have not been overlooked. Abundant use of structural formulae will be helpful to the students in grasping the subject-matter without difficulty.

A few omissions may here be pointed out. Organic fluoro compounds, which have recently sprung into prominence, have not received adequate notice. Melamine has been completely left out while recent informations on the structure of nucleic acids have been inadequately dealt with.

Inspite of these omissions, this is one of the few text-books of Organic Chemistry which may claim to be really helpful to advanced students of Chemistry. The indroduction to the method of consulting chemical literature, given at the end, has increased its usefulness. An English or vernacular translation of the book will be welcome by students in this country.

J. K. C.

Thiophene and its Derivatives.—By Howard D. Hartough. Published by Inter-Science Publishers, Inc., New York, 1952, pp. 533.

'Thiophene and its Derivatives' is the third volume of a series of monographs on 'The Chemistry of Heterocyclic Compounds'. This is the first collective review of the heterocyclic sulphur compounds, which constitute one of the most complicated branch of Organic Chemistry and this branch has developed to a voluminous extent within the past two decades.

Various phases of thiophene chemistry (both natural and synthetic) have been dealt in this monograph in a very lucid way in sixteen chapters with a bibliography in each section. These chapters comprise the discussions on the history of thiophene literature, the occurrence of thiophene and its compounds, syntheses of thiophene and its various derivatives, their physical and chemical properties, molecular structures and spectroscopy (ultraviolet and infra-red absorption spectra and mass spectra), and their biological, toxicological and pharmacological activities with sufficient literature references up to 1950. These references are well selected to facilitate access to the original publications. The book contains a large number of tables where the formulae of the thiophene compounds and valuable data on physical and chemical constants have been recorded. This is a very useful collection for research workers. Several laboratory preparations of typical thiophene compounds have been described in fair details in the appendix which will be a great practical help to the chemists who are interested in this field.

This monograph represents a detailed and comprehensive presentation of thiophene chemistry, its toxicology and pharmacology. This is the first publication of an authoritative survey of thiophene literature and it is up-to-date.

In general, the book is well written, readily understandable, and the printing good. This is a treatise rather than a text-book and as such it will undoubtedly serve as a valuable guide of the teachers, post-graduate students, research workers and everyone else interested in this field which is expanding tremendously like that of carbocyclic compounds.

A. C.

Phase Rule.—By Findlay, Campell and Smith. 9th Ed. Published by Dover Publications, Inc., New Yourk. Price $1.90.

It is highly gratifying to find Findlay's well known treatise partly revised and rewritten in its present form. The additions to the book are fairly up-to-date and in tune with the system followed in the original. The reorientation of some of the sections and even of chapters is well advised. Not having been revised by the author himself the scope of alterations is not perhaps so clear cut. Otherwise it could have been extended to further curtailment of some repetitive portions without sacrificing lucidity. Thanks to the authors of the edition under review, simplicity of the original treatment has not at all suffered in their hands. The profuse references will undoubtedly be welcome by many workers.

The thermodynamic treatment of some of the problems of phase equilibria is not quite adequate. The concept of chemcial potential, or in general of partial molal properties, has not received sufficient attention. The equation on page 19, note 4, without reference to chemical potential, which has been mentioned later in the book, remains unexplained.

The methods outlined on page 471 might well have been elaborated giving more experimental details and necessary equipments.

The drawings of figures, particularly those relating to polycomponent systems are highly satisfactory, but unfortunately the reproduction of the drawings is on varying scales; some of them seem to have been too reduced in size.

Looking at the low price of the book such shortcomings as these appear too trifle. The authors and the publishers deserve wholehearted commendation for bringing out this admirable book in an almost new and wholesome garb.

S. K. M.

Metallurgical Engineering. Vol. 1.—By Reinhardt Schuhmann Jr., Associate Professor of Metallurgy, Massachusetts Institute of Technology. Published by Addison-Wesley Press Inc. Pp. 390. Price $ 3.50.

This is a text-book written with the idea of introducing to the students the basic scientific and engineering principles common to the unit operations involved in chemical metallurgy, so as to enable them to arrive at quantitative solution of practical problems in metallurgy by the application of such principles. This is surely a departure in the right direction from the traditional method of training in metallurgy which is mainly confined to an initiation in the art of extracting metals from ores. During the last few years the chemical engineers have played a prominent role in metallurgical industry. The engineering principles common to the unit process of extractive metallurgy have therefore been thoroughly discussed in the book. The applications of the First Law of Thermodynamics in the solution of practical metallurgical problems have been extensively and lucidly explained. A successful atempt has been made in integrating the underlying principles of Physical Chemistry with metallurgical engineering. This will surely provide the students an insight into the applications of the principles in Physical Chemistry which is taught as a separate course. Typical problems bearing on the principles discussed in the volume, viz , stoichiometry, heat balance, fuels and combustion, heat and fluid flow and phase rule, have been worked out. There is besides an important chapter on refractories and metallurgical furnace construction.

B. K. M.

OBITUARY

GILBERT JOHN FOWLER

Born: January 23, 1868. Died: March 21, 1953.

GILBERT JOHN FOWLER was born in Paris on January 23, 1868. He had his early education at the Quaker School, Sidcot, Somersetshire, and obtained his B. Sc. degree in 1886 from Owen's College, Victoria University in Manchester, where he became a Demonstrator of Chemistry in 1886 and subsequently a Lecturer in the University. Here he worked till 1895. In 1896 Fowler became Consulting Chemist and later Superintendent of the Muuicipal Sewage Works of Manchester Corporation. After some years of service there he went to Germany and studied Organic Chemistry and Crystallography in the University of Heidelberg and received his Doctorate from the University in 1904. Both at Freiburg in Germany and at Sheffield in England Fowler studied metallurgy for some time. But the special subject in which he took an active and almost passionate interest from the beginning of his career was the problem of sewage disposal in cities. It turned out to be a work of lifelong interest with him and it rightly brought international reputation to him as an authority in the scientific control of sewage and trade effluents and their utilization as nitrogenous manure for the soil.

In 1906 Dr. Fowler came to India on invitation from the Government of India to deal with the problem of the purification of sewage from the population connected with the jute mills. He visited India once again in 1909 in connection with a new process for the extraction of shellac from raw materials.

Dr. Fowler developed a process for the activated sludge which constituted his most outstanding contribution on the subject. In 1912 he published a report on the treatment of sewage entering New York harbour in response to an invitation from that city. He acted as Consultant in the matter of sewage treatment to Cairo, Shanghai, Hanghai and Federated Malaya States.

In 1915 Dr. Fowler was appointed Professor of Applied Chemistry at the Indian Institute of Science, Bangalore. Since then he made India his permanent residence and home.

He served also as Professor of Bio-chemistry, Bangalore from 1916 to 1924. He retired in 1924 from his service at Bangalore and practically settled there. But in 1927 he was called to hold the office as Principal of the Harcourt Butler Technological Institute at Cawnpore. He served that Institute till 1929 in that capacity.

Dr. Fowler's scienfific work lay primarily in the field of fermentation chemistry relating particularly with the fermentative chemical changes occurring in sewage and similar waste products. A process for the production of acetone and butyl alcohol by the fermentation of sugar present in the aqueous extract of *mahua* flowers was developed by him and worked on a large scale at Nasik during the world war I. To him belongs the credit of building up a School of Bio-chemistry in India, and many of his pupils from Bangalore are now holding distinguished positions in the country. He was elected President of the Indian Chemical Society for 1928-29 and remained its Vice-President till his death. Dr. Fowler was always ready to help the Society with his advice and guidance whenever he was approached. He had been working for a long time as the Secretary (Correspondent) for India of the Royal Institute of Chemistry of Great Britain and Ireland till almost the last days of his life. His service in this capacity is an ideal of disinterested devotion, integrity and alertness. With him the sense of duty and responsibility overshadowed every other consideration, even if the work undertaken were an honorary one. He kept himself always active till the end and was a frequent contributor to many scientific and cultural journals on his favourite subject of sewage control and its utilization. He was a familiar figure in all important scientific gatherings, particularly at the annual sessions of the Indian Science Congress till only a few years before his death. He was the author of several books, of which the two best known are *Sewage Works Analyses* (1902) and *An Introduction to the Biochemistry of Nitrogen Conservation* (1934). In his later life he developed a scheme of introducing energy units or "ergs" as a currency unit for the world. He delivered lectures at several important cities in India on this subject and published his views in the form of a pamphlet under the title *Energy and Economics—A Plea for New View-point* (1941). Dr. Fowler was the technical representative of the Activated Sludge Ltd., London, for India and the Far East, a position which he held till the end of his life. He died at Bangalore on March 21, 1953.

Both as a teacher and as a man, Dr. Fowler was held in very high regard by his pupils. His relation with all his colleagues and friends were marked by cordiality and consideration. He was endowed with a placid temperament, yet he never failed to show a vivid insterest in life and humanity. By his death the Indian Chemical Society has lost one of its most distinguished Past-Presidents and well-wishers, and the profession of chemistry, a talented scholar and a teacher of great repute. He will be long remembered by his pupils and colleagues who constitute not a small proportion of the Indian scientific circle to-day. Dr. Fowler is survived by his wife and two sons.

The writer is quite conscious of his limitations in writing this obituary as he had not the privilege and pleasure of personal intimacy with Dr. Fowler. It would have been much better, if the task could have been entrusted to one of his pupils or colleagues.

P. Rây.